

CHARACTERIZATION OF ORGANIC
PARTICULATE MATTER

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Jack Suden

ABSTRACT

A study was conducted to (1) confirm and refine a procedure for determining the concentrations of primary and secondary organics and elemental carbon in atmospheric aerosols, (2) to provide a detailed characterization of such carbonaceous materials based on sampling conducted at three widely-spaced locations within California's South Coast Air Basin, and (3) to assess the impact of the study's findings on control strategies for secondary organic aerosol formation.

Employing a combination of selective solvent extraction and carbon analysis, a procedure was refined permitting analysis of two-hour particulate samples and, therefore, determination of diurnal variations of aerosol constituents. Results by this technique were compared to those obtained by high resolution mass spectroscopy.

The period sampled, four successive days in July 1975, appears to be one of stagnation for the first three days followed by the introduction of cleaner air. During this period, the composition of the carbonaceous material was similar at the three sites with clear indications of the retention of secondary organics from one day to the next. The identifiable secondary organic aerosol products corresponded primarily to oxidation products of anthropogenic cycloalkenes and open chain dienes. Gaseous aromatics and terpenes did not appear to be significant precursors to such products. Emissions of gasoline to the atmosphere by evaporation as well as gasoline combustion products are probably the dominant source of secondary organic aerosol precursors.

Substantial sampling errors were revealed in collection of particulate organics by a high-volume sampler. Recommendations for future studies include both improvements in sampling procedures and monitoring the trends in primary and secondary organic aerosols in relation to current control strategies for hydrocarbon emissions.

EXECUTIVE SUMMARY

A study was conducted concerning the carbon-containing portion of atmospheric aerosol. Such materials are of concern because of their potential health hazard (e.g., from inhalation of polycyclic aromatic hydrocarbons) and because of their ability to restrict visibility by scattering light. Carbonaceous aerosols originate from organic compounds (e.g., lubricating oils) injected into the atmosphere as fine particles (i.e., primary organics), low volatile organics formed in the atmosphere as the result of chemical reactions (i.e., secondary organics) and from elemental carbon emitted by combustion sources. In addition, particulate carbon in the atmosphere is contained in various polymeric forms (e.g., tire dust, pollen, spores) and in inorganic compounds (e.g., carbonates).

The specific goals of the current program were (1) confirm and refine a procedure for determining the concentrations of primary and secondary organics and elemental carbon in atmospheric aerosols, (2) to provide a detailed characterization of such carbonaceous materials based on sampling conducted at three widely-spaced locations within California's South Coast Air Basin, and (3) to assess the impact of the study's findings on control strategies for secondary organic aerosol formation.

Employing hi-volume filter samples collected simultaneously at Pasadena, Pomona and Riverside under conditions of moderate or light photochemical smog, the carbonaceous material was characterized both by selective solvent extraction and by mass spectrometry. Collection of seven two-hour samples and one 14-hour sample at each site permitted some assessment of sampling errors.

The composition of the particulate carbonaceous material at Pasadena, Pomona and Riverside was similar. Secondary organic carbon (C_s) generally exceeded primary organic carbon, C_p , by a factor of at least two. Elemental carbon, C_e , was, on average, the most abundant carbon form, representing about 50% of the total carbon. There was no clear indication that a particular type of class of organics contributed proportionately more to the secondary aerosols at any of the three sites.

The period chosen for sampling and analysis included what appears to be a three-day stagnation period. Evidence of retention of aerosols from one day to the next was found; specifically the aerosol collected in the early morning was relatively aged as evidenced by the extent of bromine loss. Furthermore, the secondary organic aerosols exhibited maximum concentrations prior to the time of maximum ozone concentration, consistent with its formation on preceding days.

Formation of secondary organics appears to involve reaction of gaseous cyclic olefins, materials found both in gasoline and in auto exhaust. Gaseous aromatic hydrocarbon (e.g., toluene) and reactive organics emitted by vegetation do not appear to contribute substantially to the formation of secondary organic aerosols collected in the South Coast Air Basin.

Current pollution controls (e.g., auto exhaust catalytic converters, charcoal canisters for minimizing gasoline evaporation from carburetors, gasoline station vapor recovery systems) may be expected to produce a roughly proportional decrease in secondary organic aerosols. Monitoring of atmospheric concentrations of both secondary aerosols and gasoline-related hydrocarbons periodically over the next several years is considered essential to verify this.

The study also demonstrated substantial errors in collection of carbon-containing particulates using high-volume samplers pointing to the need for improved sampling procedures. Other recommendations for further studies are included in the Technical Summary and Conclusions.

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I. Introduction

As part of the 1972-1973 ARB-sponsored Aerosol Characterization Experiment (ACHEX), considerable effort at AIHL was given to the analysis of carbonaceous material. Among other objectives, we sought to quantitate the elemental and organic carbon present and to further divide the organics into those of primary* and secondary** origin. Techniques were developed permitting such analyses on samples collected for 24-hour periods.

The foundation of these procedures was the approximation of primary organics as those organics (analyzed and expressed as carbon) soluble in cyclohexane. Secondary organics were equated with the total organics, as carbon, solubilized by extraction with benzene followed by 2:1 v/v chloroform-methanol minus the primary organics as defined above. Elemental carbon was approximated as the carbon remaining insoluble after extractions with benzene and chloroform-methanol. These procedures were supported by correlations observed between mean daytime ozone levels (as a measure of the intensity of photochemical activity) and the secondary organics, as obtained by this procedure, for ten episodes in the South Coast Basin. Primary organics, as defined here, were observed to be independent of ozone levels.

The current program has extended this work to permit analysis of the carbonaceous material collected in 2-hour and 14-hour samples. In addition, samples were collected simultaneously at three widely spaced locations in the South Coast Air Basin to permit characterization of organics both as a function of time of day and of locations.

High resolution mass spectrometric thermal analysis (MSTA) was employed both to validate the solvent-extraction approach and to provide detailed aerosol characterization. In addition, the residual filter samples following the extractions were studied by pyrolysis gas chromatography to determine, at least qualitatively, if organic carbon contributed to the estimate of elemental carbon.

To evaluate the age of the air mass studied, particulate samples were analyzed for lead and bromine. The ratio of these species has previously been used as an indicator of this parameter for aerosols with a large automobile source component. In addition, the diurnal variations of Pb and Br are useful as a tracer for automobile emissions which are believed to be an important source of primary organic aerosols.

The specific goals of the program were:

- A. To confirm and refine procedures for quantitating the primary organics, secondary organics, and elemental carbon present in atmospheric aerosols, particularly to permit measurements on 2-hour samples.

*Material injected into the atmosphere in the particulate state or in a form rapidly condensed into particles by cooling to ambient temperatures.

**Particles formed as the result of chemical reactions in the atmosphere.

- B. To provide a detailed analysis of the organic particulate matter collected at various locations in the South Coast Air Basin seeking evidence of systematic changes in average composition moving from west to east, and inferences on the structures of the gaseous precursors to such organic aerosols.
- C. To evaluate the results of this study as related to priorities for control of organic aerosol precursors.

II. Technical Summary and Conclusions

Employing hi-volume filter samples collected simultaneously at Pasadena, Pomona and Riverside, July 9-12, 1975, under conditions of moderate or light photochemical smog, the carbonaceous material was characterized both by selective solvent extraction and by mass spectrometric thermal analysis (MSTA). Collection of seven 2-hour samples and one 14-hour sample at each site permitted some assessment of sampling errors.

The solvent extraction-carbon analysis technique was refined to permit analysis of 2-hour samples with good precision. An evaluation of the selectivity of cyclohexane for extracting only primary organics from these samples indicated that while hydrocarbons are generally extracted with high efficiency, partial extraction of polar organics of probable secondary origin also occurs. Thus, the solvent extraction technique provides an upper limit value for primary organics, a lower limit value for secondary organics and an upper limit value for elemental carbon.

The carbon extractable in benzene represented about 25% of the total carbon in the samples and about half of the carbon recovered by successive benzene, methanol-chloroform extractions. The ratio of means cyclohexane/benzene soluble carbon for 14-hour samples was 0.68, which is similar to the value 0.57 observed in the ACHEX.

The composition of the particulate carbonaceous material at Pasadena, Pomona and Riverside was generally similar. Secondary organic carbon (C_s) generally exceeded primary organic carbon, C_p , by a factor of ≥ 2 . Elemental carbon, C_e , as estimated by insoluble carbon, was, on average, the most abundant carbon form, representing about 50% of the total carbon. There was no clear indication that a particular type or class of organics contributed proportionately more to the secondary aerosols at any of the three sites.

Comparisons of the diurnal variations of C_s with those for model secondary organics generally revealed similar patterns. However, comparing C_p and model primary organics, the diurnal variations, at times, differed. The partial solubility of secondary organics in cyclohexane together with the dominance of secondary over primary materials in the soluble fraction probably contributed to this. However, MSTA supported the solvent extraction-carbon analysis observation of similar diurnal patterns in C_p and C_s at Pasadena and Riverside.

The period July 9-11, 1975 appears to represent one of stagnation. Since aerosols (especially sub-micron) can be conserved from day to day but ozone beneath the mixing layer drops to nearly zero at night, a high correlation between secondary organics and ozone could not be expected. As indicators of such a stagnation period, morning Br/Pb ratios were low and the diurnal maximum in C_s and specific secondary organics preceded the ozone peak.

The present data suggest that pollutant transport and available mixing volume are important in controlling diurnal concentration changes at a given site and may, at times, dominate over emission or aerosol formation rates.

Total alkanes plus alkenes and alkylbenzenes in the aerosols appear to have a similar source. The generally poor correlation of these constituents with Pb suggests either substantial differences in rates of removal of these constituents from the atmosphere or important sources of these organics other than motor vehicles.

The identifiable secondary organic aerosol products corresponded primarily to oxidation products from anthropogenic, cycloalkenes and open chain dienes. The concentration of oxidation products from toluene, the most abundant gaseous aromatic, and from terpenes, naturally emitted reactive alkenes, was, in nearly all cases, one to two orders of magnitude below that of the major oxidation products. The principal source of both classes of anthropogenic aerosol precursors is probably from evaporation and combustion of gasoline. Current trends in pollution controls (e.g., catalytic exhaust converters, charcoal canisters for minimizing gasoline evaporation from carburetors, improved gasoline station equipment) may be expected to produce a roughly proportional decrease in secondary organic aerosols.

Finally, filter sampling of organic particulates has been shown to be subject to substantial uncertainty. Evidence of preferential loss of hydrocarbons from short-term hi-vol samples was obtained while recoveries of polar organics was greater from such samples. Low volatility carbonaceous materials are postulated to play an important role as sorbents for gaseous hydrocarbons, increasing the collection efficiency of filters for such materials with increasing loading. Loss of the polar organic particulate matter on prolonged sampling is ascribed to volatilization into air passing through the filter which is not saturated with the vapors of these materials. Thus, the routine analysis of organic aerosols (such as the total weight of benzene extractable materials) from 24-hour high-volume samples may lead to substantial error.

Further studies of organic aerosols should include:

- A. Simultaneous collection and analysis of gas phase organics, including the likely aerosol precursors, and organics collectable on a filter at widely spaced locations and at sites likely to be along common wind trajectories, especially within the Los Angeles Basin.
- B. Sampling and analysis over a period of several years to establish trends in the concentrations of the likely aerosol precursors, their corresponding products, total secondary organics and total carbonaceous aerosols.
- C. Development of improved techniques for collection of atmospheric organic aerosols.
- D. Further refinement of relatively simple techniques permitting measurement of primary and secondary organics and elemental carbon in atmospheric aerosol samples.

III. The Composition and Origin of Airborne Primary and Secondary Carbonaceous Materials (Literature Review)

A. Primary Carbonaceous Materials

It has long been believed that an important atmospheric source of urban primary organic aerosols is vehicular traffic. A study sampling aerosols adjacent to roadways concluded that the composition of the organic aerosol found resembled that of partly oxidized lubricating oils.¹ A similar conclusion was reached for cyclohexane extracts of atmospheric aerosols collected at various urban and rural sites as part of the ACHEX program.² Using column chromatography, organics extracted from auto exhaust aerosol were shown to have a composition of 31% aliphatic hydrocarbons (i.e., alkanes + alkenes), 8% aromatic hydrocarbons and 61% polar organics (i.e., materials containing O, S or N).²

Recent atmospheric sampling and analysis employing mass spectroscopy thermal analysis (MSTA) has characterized the composition of freeway-related organic aerosols as well as that of automobile and diesel exhaust. The freeway-related organics were sampled, in a single trial, upwind and downwind of a heavily traveled roadway (the Seattle Interstate 5 Freeway) during a period of "considerable freeway congestion". Aerosol was collected with a single stage impactor and glass fiber after-filter, the latter collecting particles $< 1-2 \mu\text{m}$ in aerodynamic diameter. Only the after-filter was analyzed. Table 1 summarizes the concentrations found for compounds with high downwind/upwind values. The results support vehicular traffic as an important source of particle phase alkanes, alkenes and substituted benzenes.

The MSTA results for particulate matter collected from auto and diesel exhaust are given in Table 2. As expected, the exhausts are a rich source of alkanes, alkenes and alkylbenzenes. Because of differences in sampling conditions, inferences about the effectiveness of control devices or total emissions from diesel vs. gasoline powered vehicles cannot be made from these data. It is notable that a fragment identified as "phthalates" is seen in substantial concentration in diesel exhaust and that from the automobile with the catalytic converter.* Such materials in the atmosphere might be considered to result from emissions of plasticizers (e.g., dioctyl phthalate). However, phthalates in the exhausts may result from oxidation of xylenes, dialkylbenzenes and naphthalenes present in the fuels. Phthalates were previously reported in conventional auto exhaust by Boyer and Laitinen but no quantitative assessment was made.³⁸

Diesel fuel and exhaust (gas + particle phase) have also been analyzed by GC-MS.¹⁷ A large fraction of the heavy hydrocarbons found in diesel exhaust (many of them presumably in the aerosol phase) appeared

*Under conditions in which diesel exhaust is a minor contributor to the total vehicle emissions these results imply that phthalates might provide a useful "signature" for catalyst equipped automobiles.

Table 1

MSTA OF FREEWAY-RELATED AEROSOL ($\mu\text{g}/\text{m}^3$)^a

<u>Constituent</u>	<u>Identifying Fragment</u>	<u>Upwind</u>	<u>Downwind</u>	<u>Downwind/ Upwind</u>
total alkanes	C_5H_{11}	0.58	2.2	3.8
total alkenes	C_5H_9	0.69	3.3	4.8
xylenes, alkyl benzenes	C_7H_7	0.19	0.46	2.4
alkylbenzenes	C_9H_{11}	0.15	0.61	4.2
tetrahydronaphthalene	C_8H_8	0.020	0.12	6.2
-- ^b	CONH	0.53	1.16	2.2
xylenes, ethylbenzene	C_8H_{10}	0.067	0.19	> 3
alkylbenzene	C_9H_{12}	0.16	0.22	> 3.6

a. D. L. Flugstad, Senior Thesis "The Determination of the Freeway Contribution to the Primary Aerosol by Mass Spectroscopy", University of Washington (1975).

b. While the constituent is not identifiable, CONH is the only nitrogen-containing fragment with a downwind/upwind ratio > 1.0.

Table 2

MSTA OF AUTO AND DIESEL EXHAUST
(near tailpipe) $\mu\text{g}/\text{m}^3$ ^{a,b}

<u>Constituent</u>	<u>Identifying Fragment</u>	<u>Auto^c (no converter)</u>	<u>Auto^d (with converter, idle)</u>	<u>Auto^d (with converter, high RPM)</u>	<u>Diesel bus (no converter)</u>
total alkanes	C_5H_{11}	6900	77	240	360
total alkenes	C_5H_9	6900	64	170	430
xylene, alkylbenzenes	C_7H_7	650	12	20	81
alkylbenzenes	C_9H_{11}	1500	3.3	10	124
phthalates	$\text{C}_8\text{H}_5\text{O}_3$	< 1400	730	1500	300
benzoic acid	$\text{C}_7\text{H}_5\text{O}_2$	260	66	94	0.9
xylene, ethylbenzene	C_9H_{10}	540	---	12	---
alkylbenzenes	C_9H_{12}	1660	---	---	52
tetrahydro- naphthalene	C_8H_8	92	---	8.4	24
--	CONH	350	79	---	66

a. Unpublished results, R. Knights (1977).

b. The sampling conditions are not necessarily equivalent in these studies. Thus, comparisons between the vehicles are inappropriate. However, comparisons of ratios of constituents within one sample should be valid.

c. 1.6 liter engine, Rover.

d. 5.1 liter Mercury, 1975 model.

to result from the unburned fuel. No. 2 diesel fuel was quoted to contain:

alkanes	68.3 - 85.3%
alkenes	3.2 - 4.5%
aromatics	11.5 - 28%

Additional information on gasoline and diesel powered vehicle emissions may be found in a recent book prepared by the National Academy of Sciences.²⁸

Emissions of elemental carbon and other insoluble carbonaceous particulate materials are much less well characterized. Tire dust is reported to contain about 29% carbon as elemental carbon and 58% carbon in organic compounds (the rubber itself plus oil extenders).³ Pearson, et al., have reported an SBR rubber/Pb ratio of up to 0.5 adjacent to roadways and in traffic tunnels.⁴ Pb concentrations next to roadways up to 15 $\mu\text{g}/\text{m}^3$ have been found⁵ suggesting that rubber dust concentrations should be $< 8 \mu\text{g}/\text{m}^3$. Since tire dust is expected to be in a size range where rapid fallout is significant, the level of tire dust should rapidly decrease away from vehicular traffic.

Diesel exhaust, in addition to volatile organic particulate matter, contains "soot".* The proportion of elemental/organic carbon in diesel soot is unclear.

Gasoline powered vehicle exhaust, especially from improperly functioning vehicles, may contain soot. Tebbens, et al.,^{34,35} have reported that the particulate products resulting from incomplete combustion of a variety of fuels, including low octane gasoline, benzene, toluene, hexane, cyclohexane and 1-hexene, include polynuclear aromatic (PNA) hydrocarbons as well as soot. The yields of the PNA products was noted to be low, ca 0.01% of the weight of the fuel burned. For these studies, combustion was carried out to produce black smoke by limiting the air supply. The PNA products were recovered by extraction of the collected black particulate with diethylether. The ratio soluble/insoluble carbonaceous product varied from 1:3 for 50 octane gasoline to 1:16 for cyclohexane. The insoluble product was assumed to be elemental carbon.

*A precise definition of "soot" is difficult to obtain. Thomas, et al.³⁶, have described the properties of industrial soot (e.g., channel black), airborne soot and that produced from incomplete combustion of various hydrocarbon fuels. Their model of soot is of an agglomerate of condensed polynuclear aromatic hydrocarbons with the hexagonal symmetry of graphite crystals. For example, these authors calculate that an agglomerate of ca. 4800 $\text{C}_{150}\text{H}_{30}$ molecules (i.e., 91 fused benzene rings) would occupy a volume with a diameter of 250 Å. However, all soots have associated with them volatile, lower molecular weight, soluble carbonaceous material, the amount of which varies with the source. Airborne soot particles were noted to be larger relative to industrial soot and have considerable chain structure. Carbon in such graphitic structures is here equated with elemental or inorganic carbon. The carbon in the organic solvent-soluble carbonaceous material associated with soot is here equated with organic carbon.

In addition to motor vehicles, other anthropogenic sources exist for primary organic aerosols. Cautreels, et al., employing gas chromatography-mass spectrometry, established the presence of over one hundred organic compounds in atmospheric aerosols collected in Antwerp, Belgium.⁶ Relatively high concentrations of phthalates were observed far from industrial emissions of plasticizers. Municipal waste incineration was considered by the authors to be a likely source of such emissions. As noted above, vehicle exhaust may also contribute such materials. Long chain fatty acids (e.g., stearic acid, $C_{17}H_{35}COOH$) were another significant class contributing to the organic aerosol, with even carbon numbered acids present in much higher concentrations than odd numbered ones. Combustion of organic matter of biological origin was considered to account for the higher abundance of even carbon numbered fatty acids while oxidation of unbranched alkanes was considered a source of both even and odd numbered fatty acids.

Aside from anthropogenic source of primary organic aerosols, pollens, fungi, spores and insect parts ("viable particles") should contribute to the carbon content of collected atmospheric aerosols. It is expected that relatively little of the carbon from these materials will be extracted by the solvents used in this study. Thus, such natural aerosols would contribute to the upper limit estimate of elemental carbon. A distinct diurnal variation has been reported for pollen emissions from ragweed with early morning maxima.

An extensive study to determine the protein content of atmospheric aerosols was conducted by Chambers, et al.³⁷ in 1953-55. Samples were collected at 21 locations around the United States with 24-hour high-volume samplers using glass fiber filters. The samples were first extracted with acetone to remove non-protein organic carbon; the protein was then hydrolyzed in base, ammonia (an interferent) removed and the amino acids reacted with ninhydrin. For 14 samples collected in the Los Angeles area (at Vernon and at the California Institute of Technology, Pasadena) the range in protein concentration was from 1.9 to $6.3 \mu\text{g}/\text{m}^3$. Assuming the weight percent carbon for the proteins collected to be equal to that of the amino acid, glycylalanine ($C_5H_{10}N_2O_3$), or ca. 50%, proteins contributed about 0.9 to $3.2 \mu\text{g}/\text{m}^3$ carbon to atmospheric particulates collected.

Employing carbon-14 dating techniques, Lodge, et al.⁹ were able to distinguish "contemporaneous" sources of carbon (e.g., pollen, etc. plus carbon from burning of wood, paper, garbage) from carbon of fossil origin (e.g., from combustion or aerosolization of petroleum products). Employing very large volume filter samples collected in Los Angeles, these authors found such contemporaneous carbon to represent only 15% of the ether extractable carbon but about 47% of the carbon insoluble in ether. Thus, the contribution of viable particles to the material here estimated as elemental carbon may be significant.

B. Secondary Organics

The conversion of reactive, gas phase organics to particle phase materials under simulated photochemical smog conditions has been

studied in numerous laboratories.⁹⁻¹⁵ From these studies, a reactivity scale has been constructed by the present authors as summarized in Table 3.

Cyclic alkenes (or olefins) with one or two double bonds are clearly the most efficient organic aerosol precursors. However, aromatics are also significantly reactive. Figure 1 illustrates a few of the aerosol products identified from known reactant hydrocarbons using gas chromatography-mass spectrometry. A common feature of secondary organics identified in aerosols is the presence of one or more functional groups, the effects of which is to markedly decrease the vapor pressure relative to that of a hydrocarbon of equal carbon number. Cyclic olefins, aromatics, and aliphatic dienes can yield products with two or more functional groups probably accounting for their efficient aerosol formation. Of the possible functional groups, a carboxyl group probably imparts the greatest decrease in vapor pressure thereby contributing to the importance of carboxylic acids as aerosol constituents.¹¹

It should be noted that aromatic hydrocarbons can produce both substituted aromatic and open-chain products similar to those from olefinic precursors. Identification of toluene as the precursor from the products following ring opening is especially difficult, since these consist of a series of alkenes and dienes all of which can undergo further oxidation. However, the relatively stable substituted aromatic products should provide a more readily identified indicator of organic aerosol formation from toluene.

Employing MSTA of the photochemical aerosol products from smog chamber studies with toluene, Knights, in unpublished studies, identified two fragments of high abundance, $C_7H_7NO_4$ and $C_7H_7NO_3$. The former has the same empirical formula as the aromatic product from toluene identified by Schwartz using GC-MS as shown in Figure 1. The latter may correspond to a similar compound but lacking the hydroxyl on either the side chain or the ring. Accordingly, the MSTA results in the present study were examined for evidence of these toluene products.

Natural sources of secondary organic aerosol precursors also exist. Went²³ and Rasmussen and Went²⁴ postulated that the blue haze in the Blue Ridge and Smoky Mountains resulted from oxidation of terpenes. Subsequently, Wilson, et al.¹³, studying photochemical aerosol formation from the terpene, α -pinene, identified two products, pinic and pinonic acid which were also found in aerosols sampled in the Smoky Mountains. More recent work demonstrated the formation of aerosols from limonene and terpinolene¹⁴, both by reaction with ozone and under irradiation in the presence of NO_x .

The degree to which natural aerosol precursors may contribute to aerosols observed in urban areas is unclear. Employing ACHEX particulate samples collected at West Covina, Cronn, et al.²⁵, provided tentative identification of a series of terpene oxidation products.

Table 3

APPROXIMATE REACTIVITY SCALE FOR ORGANIC AEROSOL FORMATION
(in order of decreasing reactivity)

cyclic alkenes (or olefins)

aliphatic dienes

alkylbenzenes

> C₆ aliphatic alkenes

< C₆ alkenes

alkanes

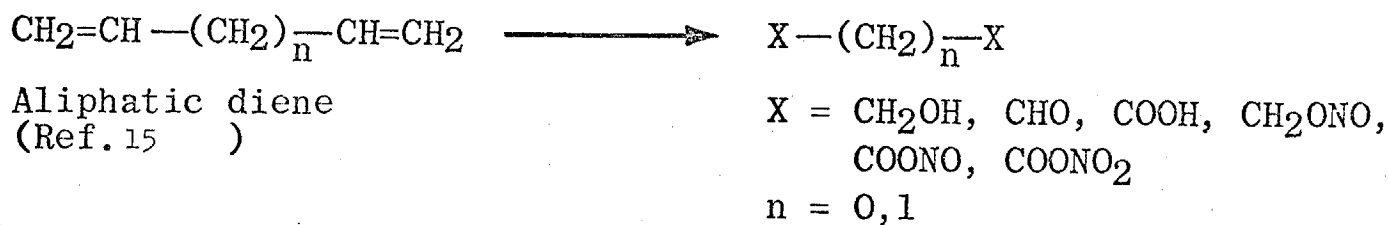
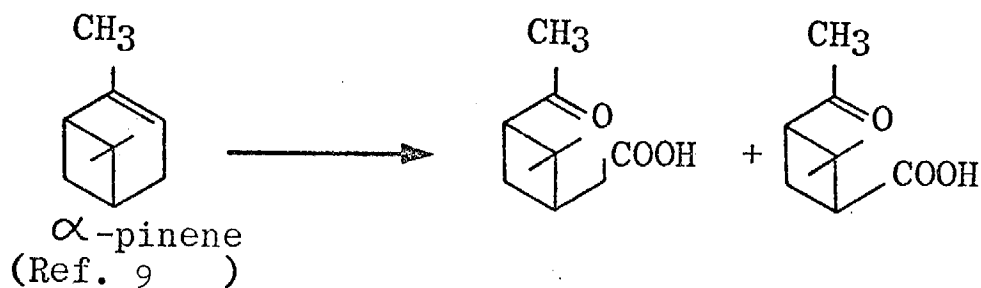
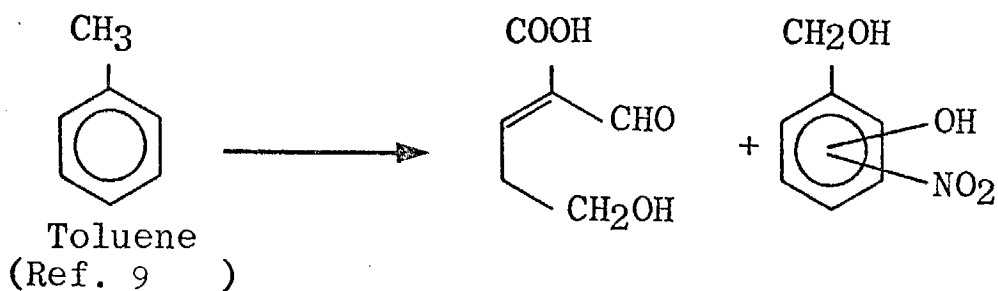
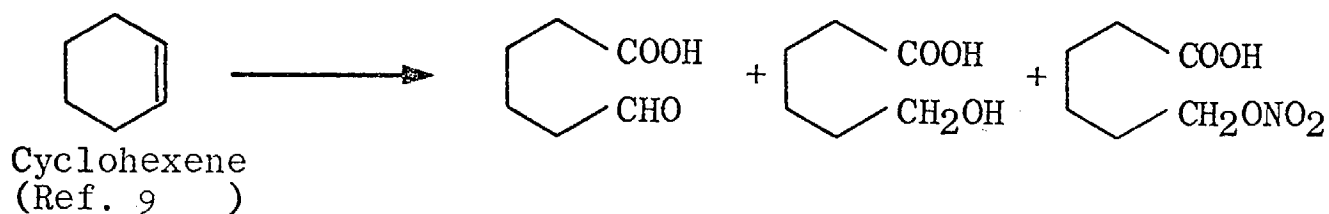


Figure 1

TYPICAL AEROSOL-FORMING REACTIONS OF HYDROCARBONS
 UNDER SIMULATED PHOTOCHEMICAL SMOG CONDITIONS

Compounds suggested and their identifying mass fragments are as follows:

pinonic acid ($C_{10}H_{16}O_3^+$)

pinic acid ($C_9H_{12}O_4^+$)

$C_{10}H_{16}O_2$ isomer

$C_{10}H_{14}O_3$ isomer

$C_9H_{14}O_2$ isomer

These materials showed an afternoon (1220-1420 PST) maximum in concentration with the total of all the above of about $1 \mu g/m^3$. On the day sampled, the total carbon during this time period was $47.6 \mu g/m^3$. Thus, the tentatively identified natural aerosol represented about 2% of the total particulate carbon at this site and time period.

C. The Concentration of Hydrocarbon Aerosol Precursors in the Atmosphere

Considering the degree of knowledge presently available on the composition of organic aerosols and the probable hydrocarbon precursors, relatively few data exist on the actual concentrations of such precursors in the atmosphere. Auto exhaust and evaporation of unburned gasoline probably represent the most important sources of anthropogenic secondary aerosols precursors. Reference 16 identified 180 compounds in gasoline many of them being $\geq C_5$ olefins or aromatics. For example, cyclohexene and cyclopentene were reported to be present at 0.1 and 0.03% w concentrations, respectively, in regular grade gasoline. Benzene and toluene were present at 1.4% w and about 6% w, respectively, in this gasoline.¹⁶ In addition, 1-methylcyclopentene, 3- and 4-methylcyclohexene were also identified in gasoline. Since gasolines must have an upper boiling point of $< 400^\circ F$, all these components would probably exist in gas phase under ambient conditions. Combustion leads to emission of partly dehydrogenated hydrocarbons in auto exhaust.³² For example, using as the fuel isooctane (2,4,4-trimethylpentane), 2-methyl-1,3-butadiene and 2-methyl-2,3-pentadiene were identified as minor exhaust products. With a pure aromatic hydrocarbon, m-xylene, as the fuel, the exhaust contained minor amounts of toluene as well as 1-methyl-3-vinylbenzene.

Several surveys of the atmospheric gaseous hydrocarbon concentrations in the Los Angeles Basin have been made.^{18-21,28,33} Altshuller, et al.¹⁸, noted a diurnal maximum in gas phase alkylbenzenes around 0800 (PST), consistent with a motor vehicle origin and with the importance of these as aerosol constituents in auto exhaust, as previously noted. At downtown Los Angeles, alkylbenzenes and toluene concentrations up to ca. 125 ppb and 45 ppb, respectively, were observed. Stephens reported an atmospheric cyclopentene concentration of 4.4 ppb.²² Complete conversion of this to pentanedioic acid would produce about $24 \mu g/m^3$ of the acid, primarily in the aerosol form.

The most important known natural aerosol precursors are terpenes, which are open chain or cyclic alkenes and dienes. Data relating to terpene emissions from plants have come from Rasmussen and Went²⁸

and Rasmussen.²⁷ The latter reference notes that 92% of the trees found in Pacific Coast Forest Regions are terpene emitters. Aside from α -pinene, terpenes identified include isoprene, cineole, limonene, α -terpinene and p-cymene. Only limited terpene concentration data are available. For example, concentrations up to 24 ppb isoprene were observed above mango leaves in Panama.²⁷ No reliable data have been obtained in the LA Basin, to our knowledge.

The terpenes probably exist both in gas phase, and in particle phase adsorbed on other materials. The MSTA technique does not, unfortunately, provide a unique determination of any of these materials.

IV. Field Sampling

A. Sampling Strategy

Two hi-volume samplers were positioned 2-3 meters apart at each of three locations:

1. Pasadena (roof of Keck Laboratory, Cal Tech)
2. Pomona (roof of Pomona Station of the SCAPCD-MZ)
3. Riverside (roof of the ARB Research Van parked adjacent to the Fawcett Laboratory, UC-Riverside)

In addition, provisions were made to secure O₃ data from DASIBI UV or REM chemiluminescent analyzers installed at the same locations during the periods when particulate samplers were being operated.

Two hi-vol particulate samplers were operated simultaneously at all locations for eight days during July 1975. One hi-vol at each site operated continuously for 14 hours (0700-1900 PDT) while on the second hi-vol, filter changes were made at 2-hour intervals throughout the same 14-hour period. At Pasadena, the operator calculated 2-hour average O₃ concentrations from 60 determinations made at 2-minute intervals. At Pomona, the usual 1-hour average O₃ values were obtained as read by the district station operator. At Riverside, instantaneous O₃ values recorded on magnetic tape at 15-30 minute intervals were transmitted to AIHL for subsequent calculation of 2-hour average values.

Particulate sampling was done with 8 x 10" Gelman AE filters which had been pre-extracted, in batches of 20-25 filters, for 18-24 hours in 2:1 v/v chloroform-methanol in a large Soxhlet extractor and heated overnight at 450°C in air. Pre-extraction was necessary to reduce the carbon blank values. Filters were preweighed after equilibration to ambient humidity.

Calibration of samplers and logistics for field sampling are detailed in Appendix A.

B. Description of Days Sampled

Table 4 summarized the maximum O_3 and, for Pasadena, the maximum in light scattering coefficient, b_{scat} , for each of the days sampled. The intention was to select four days which exhibited substantial photochemical smog and which provided what were considered typical meteorological conditions (i.e., transport of pollutants eastward to Riverside from the western part of the Basin).

Aside from the data shown in Table 4, an assessment of pollutant transport on the days sampled was made with the cooperation of Meteorological Research, Inc. An AIHL staff member, working under supervision of Stan Marsh, MRI, compiled all available wind speed and direction data for each of the days sampled at 4-hour intervals: 0800, 1200, 1600 and 2000 hours PDT. Since there was generally little difference in wind trajectories at 1200 and 1600, Figures 2-9 present the resulting surface afternoon winds map for just the 1600 hours data.

These figures suggest the following:

1. On all sampling days, the onshore flow would result in afternoon transport of pollutants toward Pasadena, Pomona and Riverside from points to the west and southwest.
2. Afternoon transport of pollutants from Pomona to Riverside occurred on July 8 and 9 but probably not on the remaining days.
3. No transport of pollutants from Pasadena east is indicated.

Based upon the intensity of the photochemical smog, pollutant transport and the desirability of analyzing samples on successive days, the July 9, 10, 11 and 12 episodes were selected for analysis at AIHL. The July 9 and 10 episodes were selected for analysis by MSTA. A number of samples from July 16 were also analyzed at AIHL.

Table 5 includes additional meteorological data for the episodes analyzed as well as the day preceding. The July 9-12 episodes were characterized by restricted vertical mixing, temperatures from 27 to 32°C with minimum meteorological ranges (at Pasadena), calculated from b_{scat} values³⁰, from 9.6 to 28 km. Pollutant levels were relatively high except on July 12.

During the period July 7-12, 1975, a low pressure region was centered over southeastern California or Arizona producing a generally northerly air flow pattern in Southern California. However, the surface wind direction within the South Coast Air Basin was apparently dominated by the diurnal land-sea breeze. Surface wind data at 4-hour intervals for all sampling days are included as Appendix B. The diurnal trends in surface winds were quite similar on the four days analyzed excepting for July 12. On this day, the 0800 PDT wind map indicates a northwesterly wind flow in contrast to a north-northeast pattern on the other days at this time period.

Table 4

DESCRIPTION OF DAYS SAMPLED

<u>Date</u>	Max. O ₃ (ppm)			Max. b _{scat} at <u>Pasadena^{a,e}</u>	Inversion Height, 10 ² ft <u>Downtown LA^c</u>
	<u>Pasadena^a</u>	<u>Pomona^b</u>	<u>Riv.^{a,d}</u>		
7/8/75	.14	.24	.21	2.8	19
7/9/75	.38	.34	.18	4.9	23
7/10/75	.30	.28	.19	3.0	25
7/11/75	.28	.36	.22	3.5	28
7/12/75	.13	.15	.15	1.7	22
7/14/75	.17	.17	.15	2.1	32
7/15/75	.21	.22	.16	2.2	27
7/16/75	.23	.18	.15	2.5	25

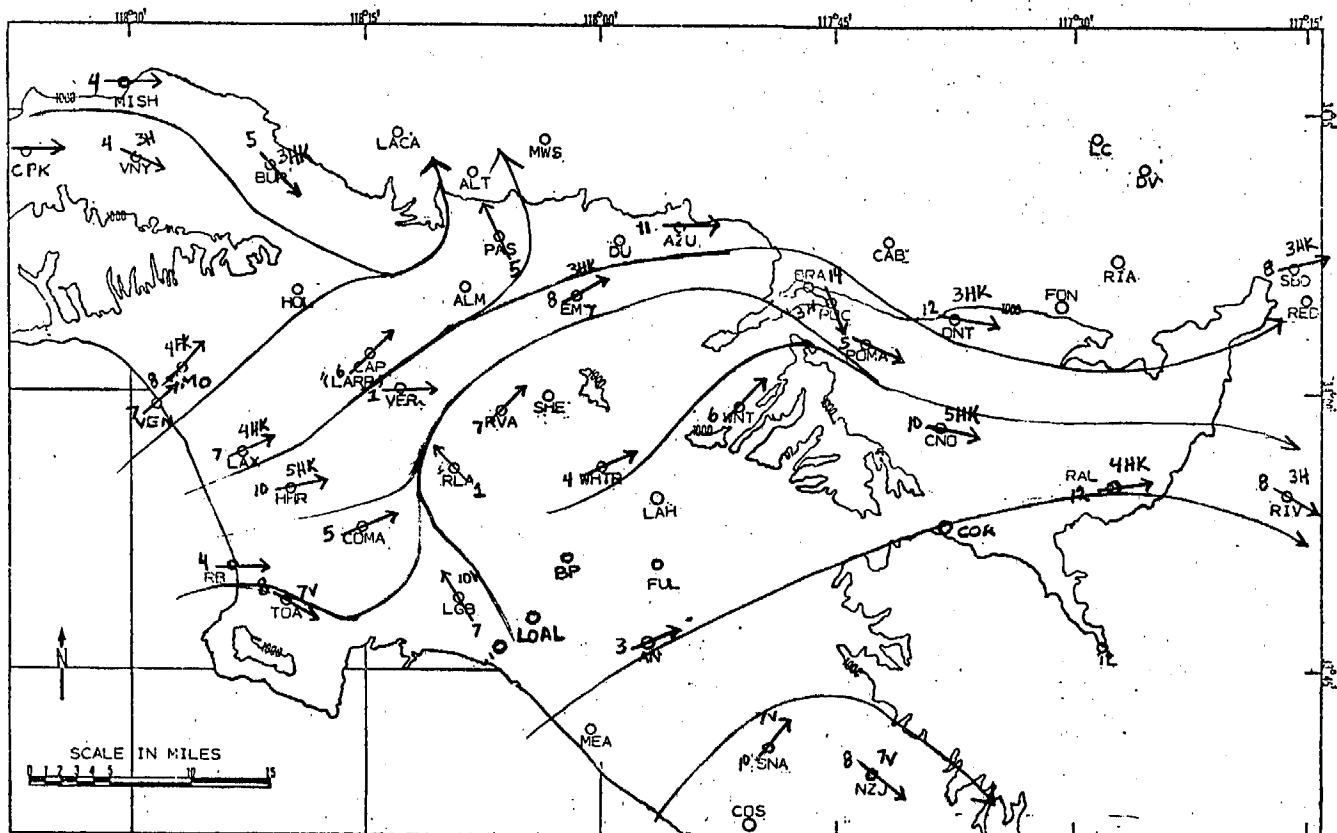
a. Highest 2-hour average

b. Highest 1-hour average

c. Calculated maximum inversion base height, downtown Los Angeles based on 0600 PST sounding at LAX. Taken from "Air Quality and Meteorology", Vol. XX, No. 7, Air Pollution Control District, County of Los Angeles, July 1975.

d. Values corrected to UV calibration base.

e. Units are 10⁻⁴ m⁻¹

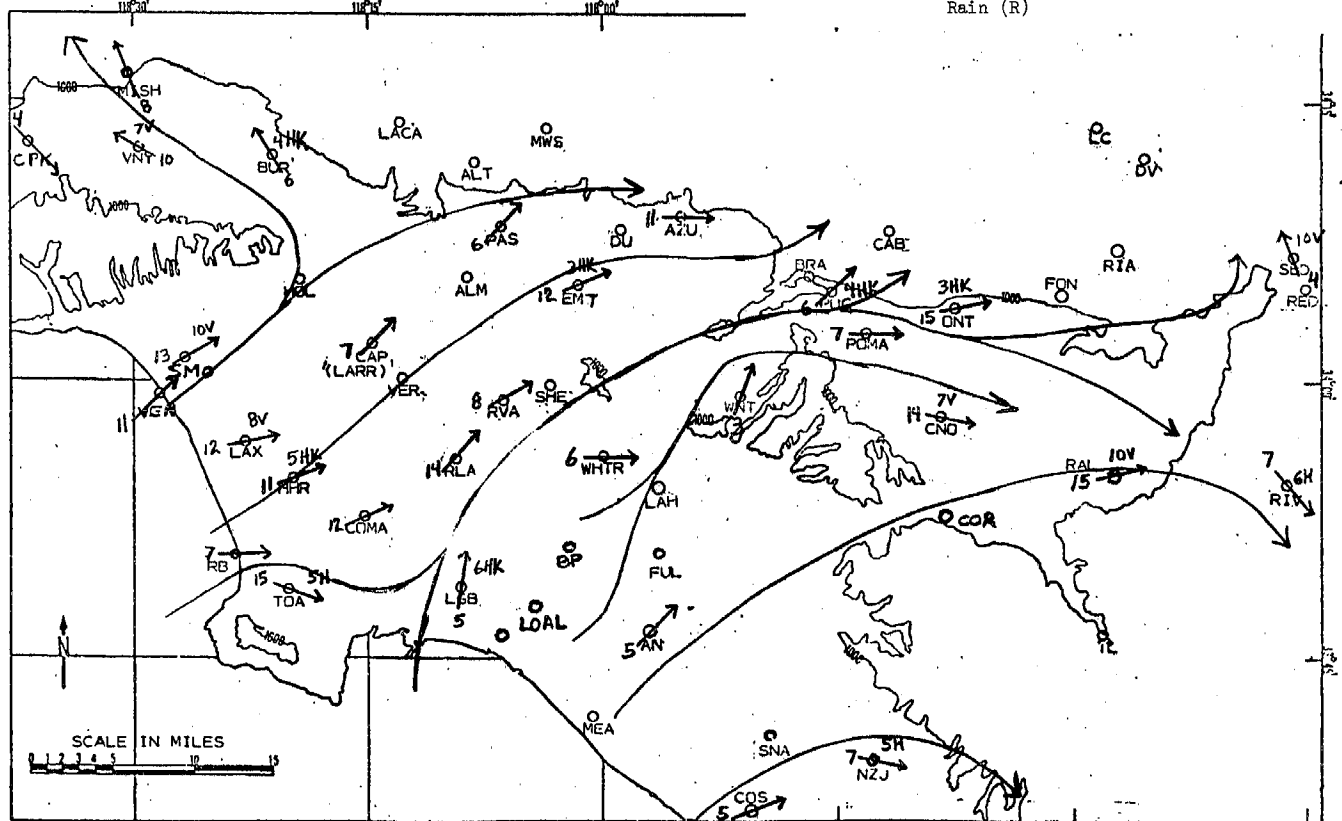


1600 PDT July 9, 1975

Figure 2

Key to Meteorological Data

n → n = windspeed in mph with arrow noting direction
 m = visibility, in miles
 x = Fog (F)
 Haze (H)
 Smoke (K)
 Rain (R)



1600 PDT July 9, 1975

Figure 3

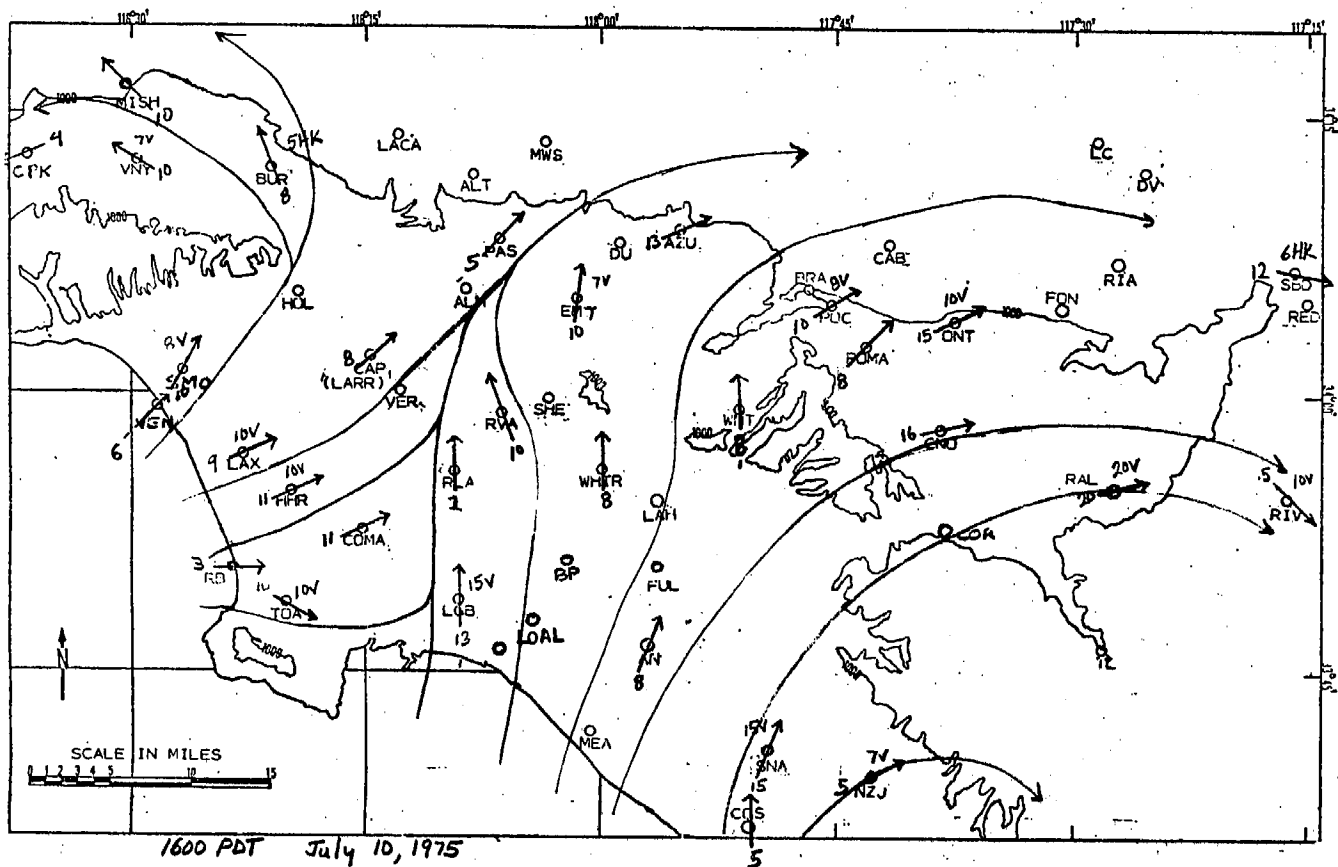


Figure 4

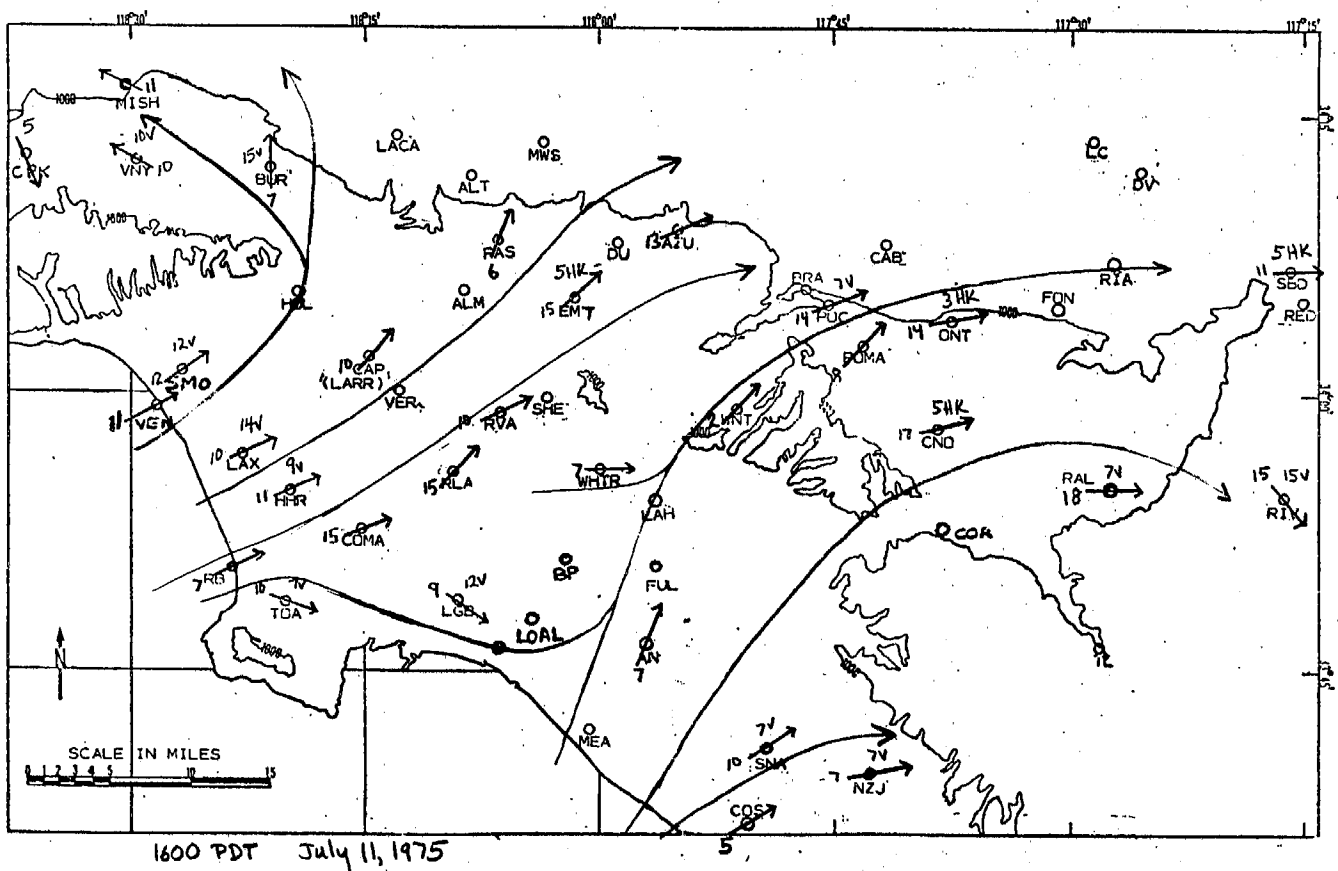


Figure 5

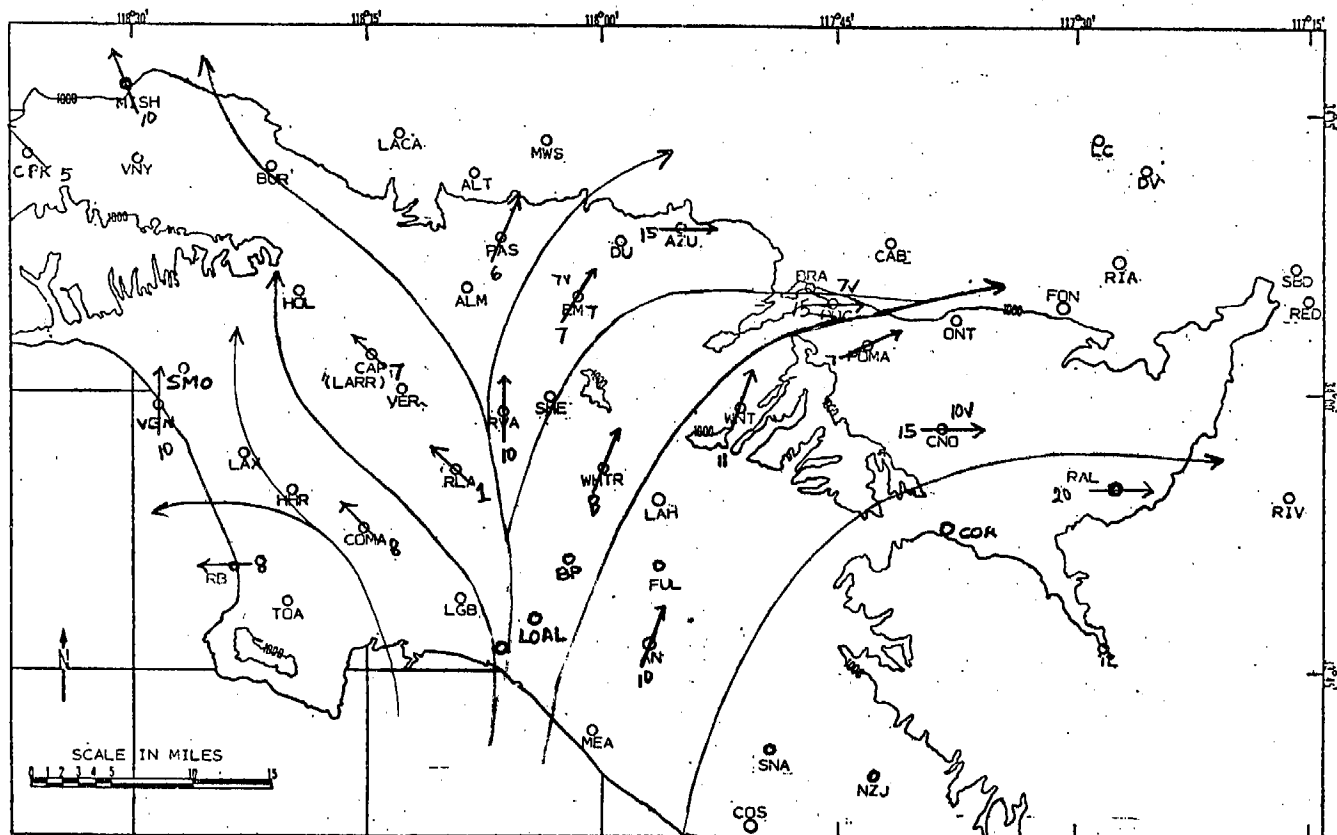


Figure 5

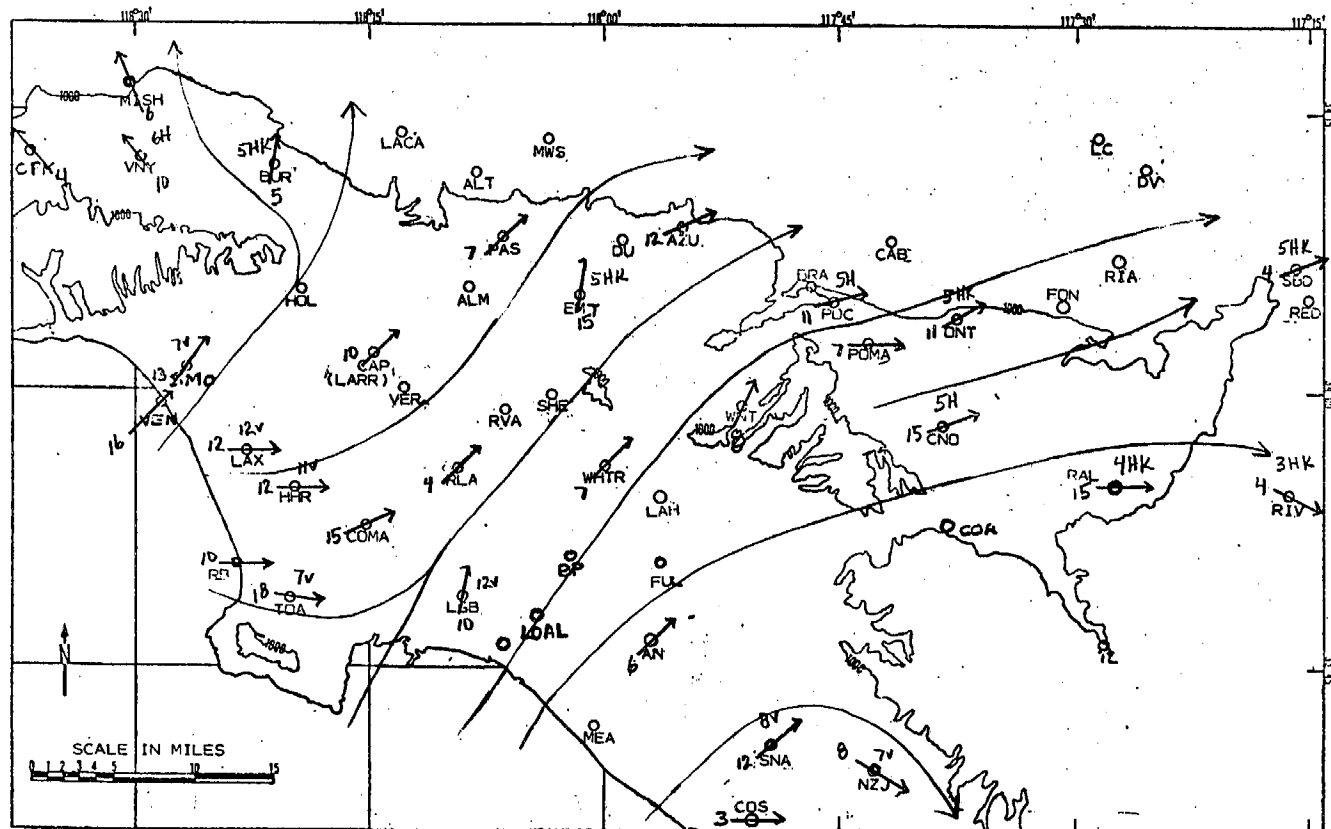


Figure 7

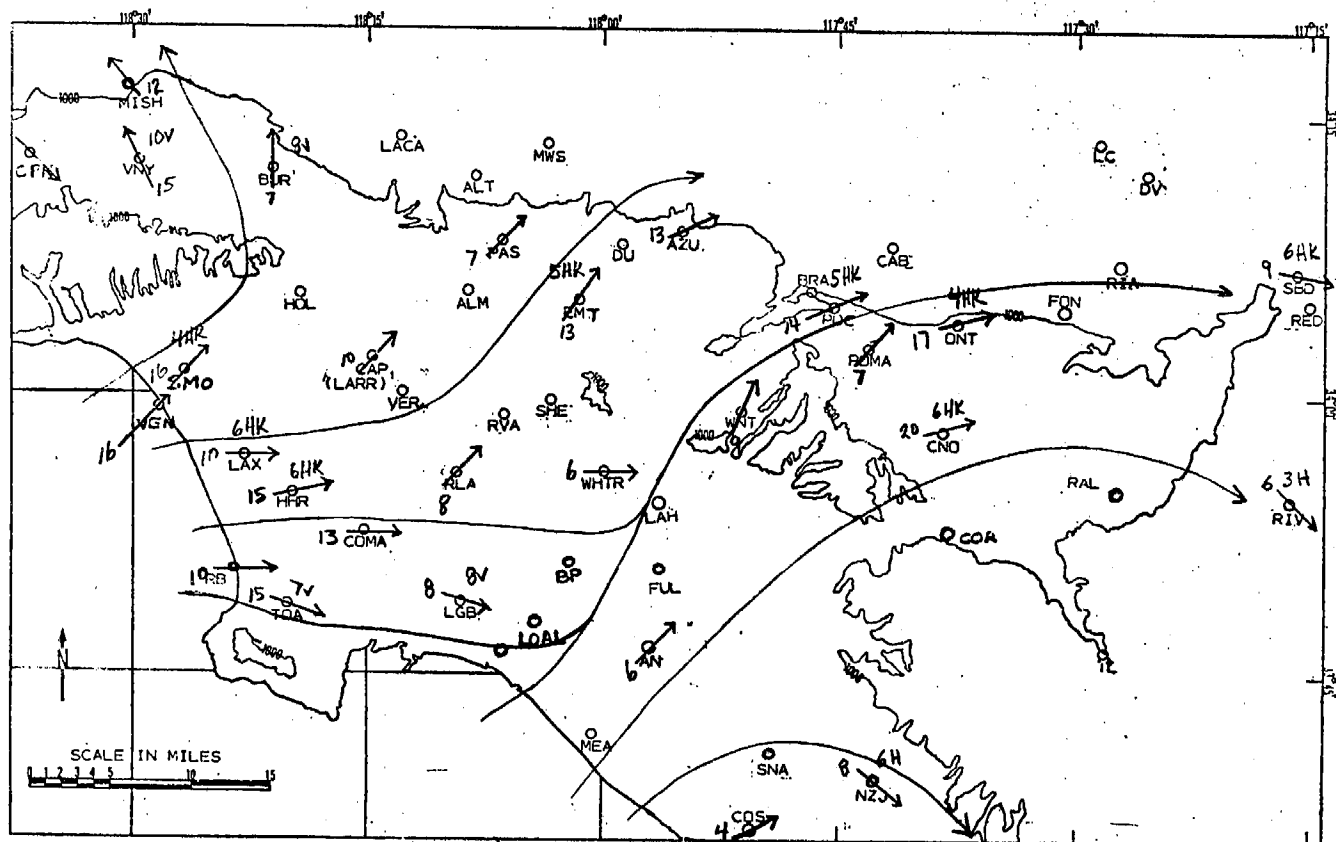


Figure 8

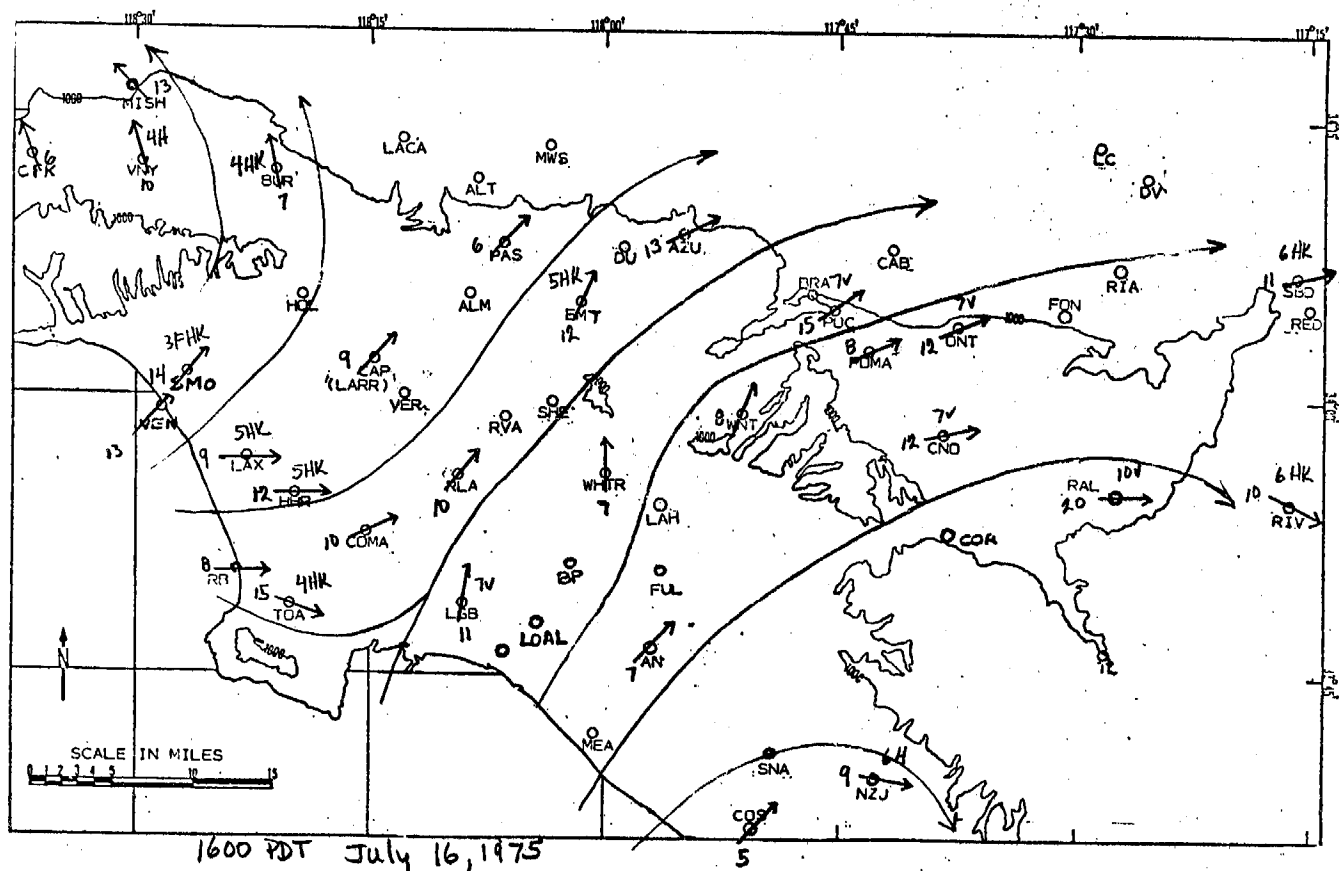


Figure 9

Table 5

SUMMARY OF METEOROLOGICAL AND VISIBILITY OBSERVATIONS

Date	Episode Designation	Mixing Height, at Noon, ^d El Monte	Inversion Strength, El Monte	Two-hr. Ave. Max bscat (10 ⁴ m ⁻¹)	Time of Maximum bscat(PDT)	Maximum ^b Temp. °C	Max/min R.H. %
7/8/75	A	1670	strong	2.8	1300-1500	26	87/63
7/9/75	B	1800	weak	4.9	1100-1300	27 ^c	---
7/10/75	C	2260	weak	3.0	1100-1300	32	74/39
7/11/75	D	1180	weak	3.5	1100-1300	32	68/32
7/12/75	E	not available ^e	---	1.7	0900-1100	28	87/53

a. At Pasadena

b. At Los Angeles Civic Center

c. National Weather Service predicted value.

d. Feet above mean sea level.

e. Based on a noon mixing height at Los Angeles International Airport of 1740 feet (strong inversion), a mixing height at El Monte > 3000 feet is expected.

V. Analytical Strategy

A. Solvent Soluble Carbon

In the organic analyses previously carried out for the ACHEX with 24-hour hi-vol samples, 8 x 10" filters were cut in half, one-half extracted with cyclohexane and the second half extracted successively with benzene and 2:1 v/v chloroform-methanol. All extractions were done in Soxhlet extractors following which the extracts were evaporated to dryness on a steam bath in a tared 25 ml flask. After drying, these were weighed to determine the total weight of extractable organics. Then, an aliquot of the oily residues was transferred to a preweighed boat, weighed and analyzed for carbon by combustion. This procedure was limited principally by the precision in weighing the 25 ml flask and the possible inclusion of suspended (rather than dissolved) material in the weight of extract.

In the current program, the need for weighing the extract was eliminated; extracts were reduced to a known volume (10 or 25 ml) an aliquot transferred to a pre-fired porcelain boat, evaporated to dryness and analyzed for carbon.

The schemes for sectioning of filters and extraction of the resulting sections are given in Figures 10, 11 and 12. Details of these analytical procedures are given in Appendix C. Extensive studies were conducted to establish limits of detection, precision, accuracy and errors due to volatile losses. These are included in Appendix D.

B. Total Non-Carbonate Carbon Determinations

One-inch discs cut from the filters were analyzed for carbon as described in Appendix C.

C. Carbonate Carbon Determinations³¹

The technique used to estimate elemental C includes all carbon insoluble in benzene and in methanol-chloroform. However, this fraction includes, besides elemental C, carbonate C and carbon in various polymers. Based upon previous work², it was expected that carbonate C would be a minor contributor. Nevertheless, a 1" disc from each 14-hour filter was analyzed for carbonate C. In the technique employed, the sample was reacted with a 5% phosphoric acid solution at 50°C. The evolving CO₂ was collected and analyzed in the same way as for the other carbon determinations. Validation of this technique is discussed in Appendix D.

The carbonate carbon values found for the 14-hour samples of this study were not significant, representing < 2% of the insoluble carbon. Therefore, no carbonate C correction to the elemental C estimate is considered necessary.

Figure 10. SECTIONING OF 8"x10" FILTER SAMPLES FOR ANALYSIS

FILTER HALF FOR CEC

FILTER HALF FOR BEC + MCC

Legend

CAC = Carbonate C
CEL = Total non-carbonate C
MSTA = Mass spec thermal analysis
XRFA = X-ray fluorescence analysis
CEC = Cyclohexane extractable C
BEC = Benzene extractable C
MCC = Methanol-chloroform extractable C

Distance from Filter to Aliquot Centers (inches)

Pb, Brand Reserve	5/8
MSTA	1 7/8
CEL	3 1/8
CAC	4 3/4

Figure 11. FLOW SCHEME - 2 HOUR FILTER SAMPLES

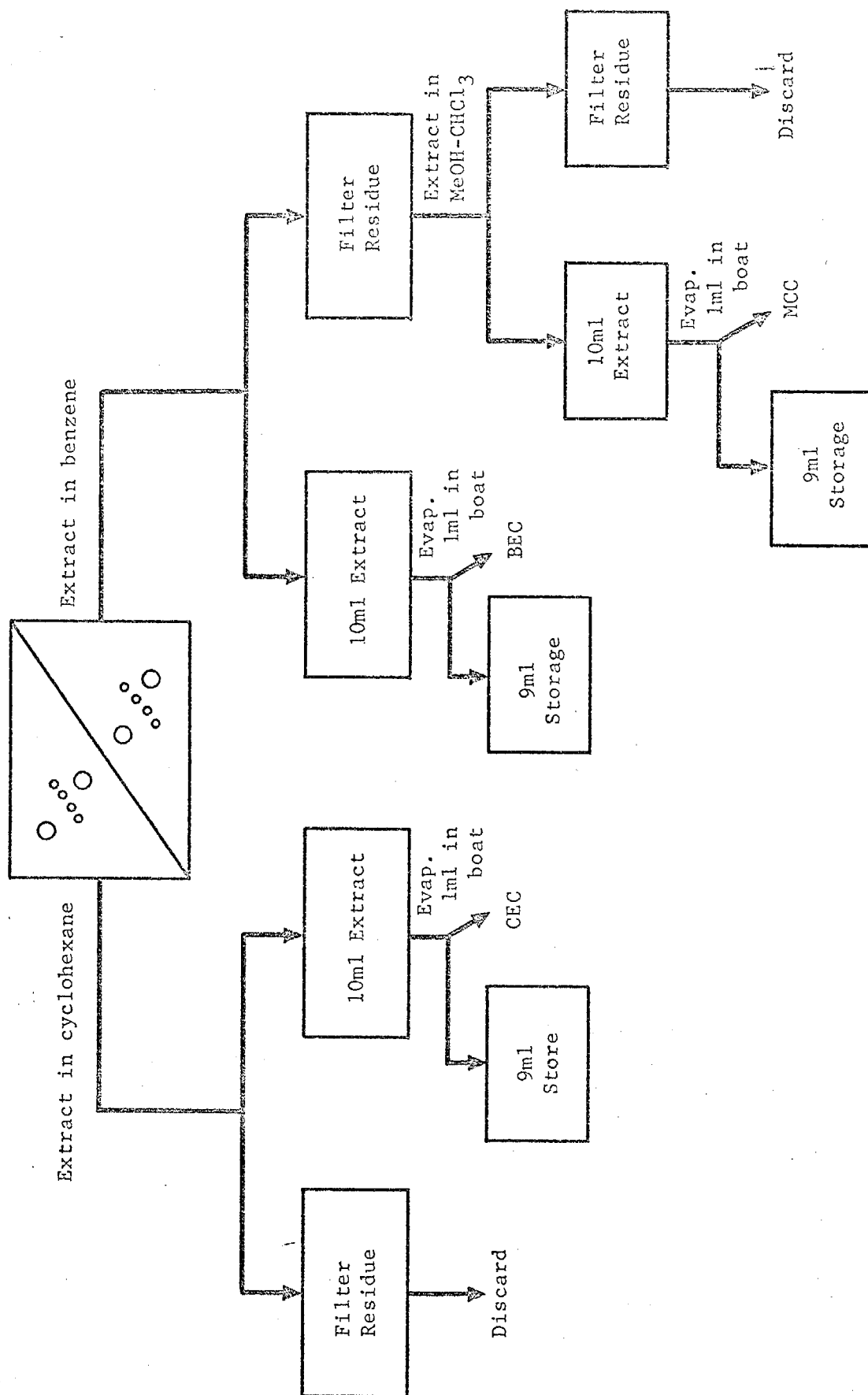
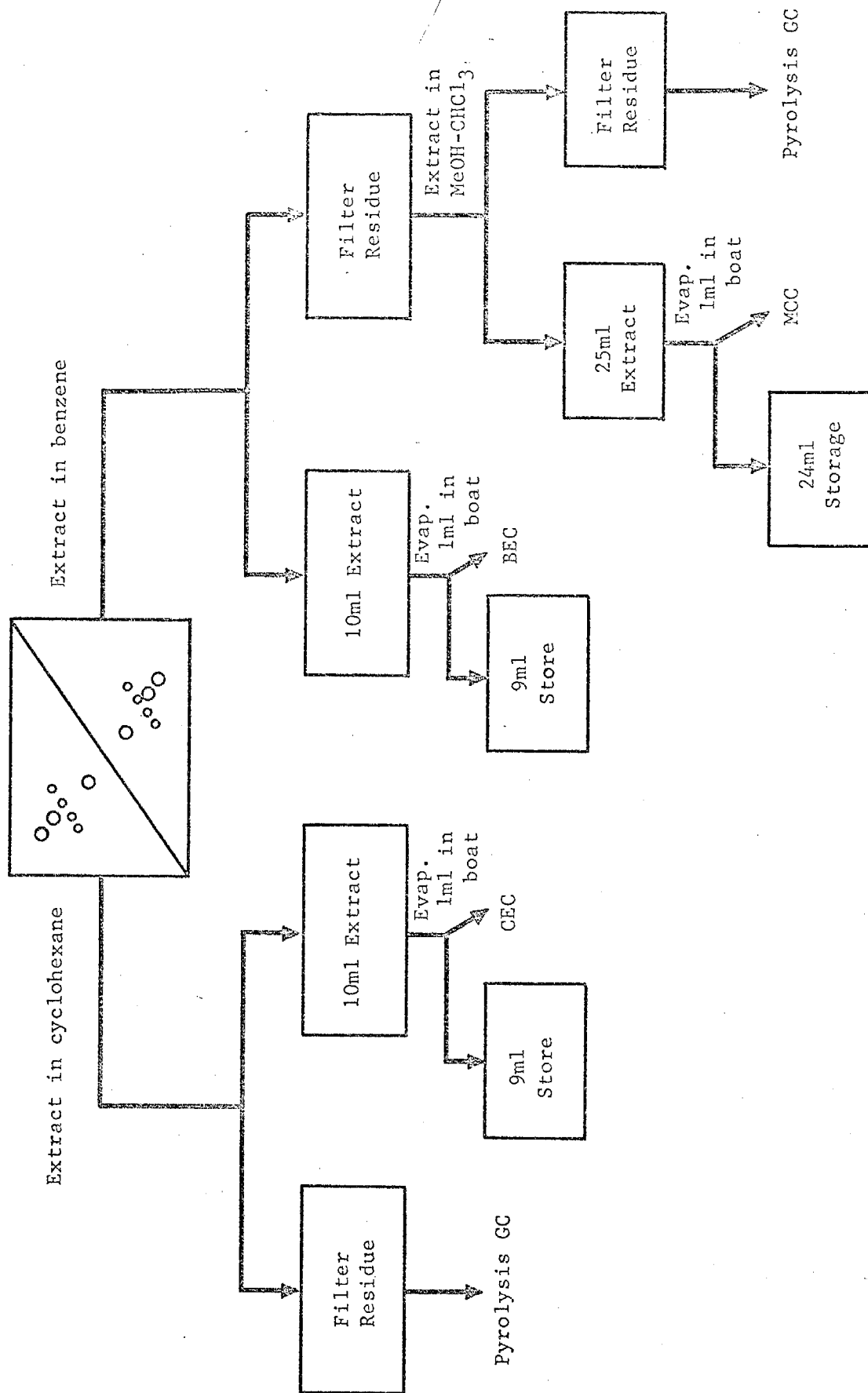


Figure 12. FLOW SCHEME - 14 HOUR FILTER SAMPLES



D. Mass Spectrometric Thermal Analysis (MSTA)

In this technique, small glass fiber filter sections representing particulates from 0.2 to 3 m³ of air are placed in a temperature programmed inlet system of a high resolution mass spectrometer. The temperature increases linearly with time to about 380°C with the volatile components vaporizing from the sample at their characteristic temperatures. The instrument scans through all mass numbers periodically to obtain mass thermograms, which are the changing intensity of mass fragments as a function of temperature. Use of temperature programming reduces the complexity of the spectra. High resolution mass spectrometry can identify mass fragments with sufficient accuracy to assign elemental compositions to these observed molecular fragments present in particulate matter. Molecular structures are assigned based upon fragment abundance patterns of known compounds expected, or verified by more specific methods (e.g., gas chromatography-mass spectrometry or GC-MS).

Most compounds are identified by their most abundant fragment, as indicated in Table 6. Mass spectral analysis often does not distinguish between different molecular isomers of the same elemental composition. Many mass fragments are, therefore, identified only as "Isomers" of some elemental composition. Some are identified as a compound "+ Isomers" when other isomers or other compounds are likely to contribute to that mass.

Quantitative calculations convert measured area under a mass thermogram for an identifying mass fragment into concentration as follows:

$$\text{Conc } (\mu\text{g}/\text{m}^3) = \frac{(\text{Area under mass thermogram})}{(\text{Response Factor}) \left(\frac{\text{m}^3}{\text{Analyzed}} \right) (\text{Instrument Sensitivity})}$$

The response factor is the measured area per microgram relative to a standard (ortho-bromobenzoic acid). The response factor is, for many compounds, the largest source of systematic error, because it is often obtained from literature values or is estimated from similar compounds. Most concentration results are expected to be accurate within a factor of two, as limited by the response factor. An inaccurate response factor will multiply all concentration results for a given compound by the same value, which will not change the appearance of diurnal profiles or the comparisons among samples.

The precision of the method was established by replicate determinations on separate days with three samples. For compounds present at > 0.1 $\mu\text{g}/\text{m}^3$, the mean coefficient of variation was 46%. Below 0.1 $\mu\text{g}/\text{m}^3$, the mean C.V. was 51%. Samples were analyzed in sets with all filters from a given site and episode being analyzed on one day. The precision for repetitive samples on the same day was not determined. However, inspection of diurnal patterns suggests C.V. values well below those cited above. Quality assurance studies, including precision, comparison of organics recovered by MSTA and solvent extraction and minimum detectable concentrations are included in Appendix D.

Table 6

IDENTIFICATION OF AIR POLLUTANTS BY MSTA

<u>Identifying Fragment</u>		<u>Compound Name</u>	<u>Relation to Molecular Formula^a</u>	<u>Response Factor^b</u>
<u>Mass</u>	<u>Formula</u>			
71.0860	C ₅ H ₁₁	Total alkanes	M-R	11.3
69.0704	C ₅ H ₉	Total alkenes	M-R	11.3
91.0548	C ₇ H ₇	Xylenes, Alkylbenzenes	M-R	17.5
106.0782	C ₈ H ₁₀	Xylenes, Ethylbenzenes	M-R	8.0
119.0860	C ₉ H ₁₁	Alkyl(C4+)-benzenes	M-R	10.0
120.0938	C ₉ H ₁₂	Alkyl(C3)-benzenes	M	7.8
104.0626	C ₈ H ₈	Tetrahydronaphthalene	M-C ₂ H ₄	6.8
138.1408	C ₁₀ H ₁₈	Perhydronaphthalene	M	3.2
145.1018	C ₁₁ H ₁₃	Dimethyltetrahydronaphthalene	M-CH ₃	8.8
86.0368	C ₄ H ₈ O ₂	Pentanedioic Acid	M-CH ₂ O ₂	0.45
100.0524	C ₅ H ₈ O ₂	Hexanedioic Acid	M-CH ₂ O ₂	0.38
122.0366	C ₇ H ₆ O ₂	Benzoic Acid	M	8.0
149.0238	C ₈ H ₅ O ₃	Phthalates	M-ROR+H	1.0
43.0058	CONH	Organic Nitrates and Nitrites	M	1.0
		N-containing organics	M-?	1.0

a. M-R means identifying fragment obtained by loss of alkyl (R) from unfragmented molecule (M).

b. The Response Factor of a compound relative to the quantitative standard, ortho-bromobenzoic acid.

E. Pyrolysis Gas Chromatography-Mass Spectroscopy

A small number of samples were analyzed by pyrolysis gas chromatography-mass spectroscopy. In this technique, high molecular weight organic compounds are heated at 450°C, under nitrogen, to produce thermal cracking resulting in formation of volatile organic materials. These volatile organics are then separated by GC and identifications confirmed by MS. Inferences are then made about the composition of the original sample.

The filter samples analyzed had already been extracted with benzene and methanol-chloroform or cyclohexane. The intention was to obtain at least qualitative information about the organics remaining on filter samples after these extractions.

VI. Validation of the Solvent Extraction Technique

A. MSTA of Solvent Extracts

As part of the effort to validate the selective extraction technique, cyclohexane, benzene and methanol-chloroform extracts from 14-hour filter samples were analyzed by mass spectrometric thermal analysis (MSTA). Assuming negligible decomposition during extraction, these analyses, while limited in precision, could provide a direct measure of the selectivity of the solvents, used for atmospheric samples. For interpretation of results, the sum of alkanes and alkenes as well as alkylbenzenes were used to represent primary organics; hexanedioic acid, pentanedioic acid and total difunctional organic nitrates + nitrites were used to represent secondary materials. These results are compiled in Table 7. We first note that cyclohexane and benzene appear, on average, to be equivalent for the extraction of alkanes and alkenes; for the July 9th episode, the ratio of means cyclohexane/benzene was 1.0 for analysis of these materials. Additional extraction with methanol-chloroform recovered only about 10% of the alkanes + alkenes extracted into benzene. For alkylbenzenes, benzene recovered about three times the concentration observed in cyclohexane.

Inspection of the results for the secondary materials indicates relatively high concentrations in cyclohexane. Thus, these results do not appear to support the hypothesis made for selective extraction of primary organics by cyclohexane. However, increased perspective is obtained by comparing results for organics recovered by extraction in benzene followed by methanol-chloroform with results for analysis of the corresponding filter. Table 8 shows this comparison from which one can conclude:

1. Recovery of alkanes plus alkenes is greater by extraction relative to direct filter analysis.

Table 7

MSTA ANALYSIS OF PARTICULATE EXTRACTS FROM 14-HOUR SAMPLES ($\mu\text{g}/\text{m}^3$)^a

Episode (1975)	Site ^b	Solvent	Alkanes + Alkenes	Alkyl- benzenes ^e	Hexanedioic Acid	Pentanedioic Acid	Organic Nitrates + Nitrites ^c
July 9	Pa.	cyclohexane	1.31	0.13	1.0	0.0	0.16
July 9	Pa.	benzene	1.29	0.34	1.2	0.58	0.063
July 9	Pa.	MC ^d	0.12	0.027	0.13	0.21	0.011
July 9	Po.	cyclohexane	1.02	0.16	0.11	0.054	0.047
July 9	Po.	benzene	1.74	0.48	0.43	0.34	---
July 9	Po.	MC	0.063	0.032	0.18	0.14	---
July 9	Riv.	cyclohexane	0.63	0.13	0.47	0.15	---
July 9	Riv.	benzene	0.66	0.20	0.47	0.18	0.020
July 9	Riv.	MC	0.03	0.060	0.19	0.30	---
July 10	Pa.	cyclohexane	0.98	0.16	1.0	---	---
July 10	Po.	cyclohexane	1.05	0.09	0.29	---	0.022
July 10	Riv.	cyclohexane	0.42	0.16	0.18	---	---

a. One half of filter extracted with cyclohexane, the second half extracted successively with benzene followed by methanol-chloroform.

b. Pa. = Pasadena, Po. = Pomona, Riv. = Riverside

c. Includes C₅-C₇ aldehyde nitrates and acid nitrates and/or nitrites

d. 1:2 v/v methanol-chloroform

e. The sum of those detected by fragments C₇H₇, C₈H₁₀, C₉H₁₁ and C₉H₁₂

Table 8

COMPARISON OF MSTA OF EXTRACTABLE ORGANICS AND FILTER SAMPLES^{a, b} ($\mu\text{g}/\text{m}^3$)

Site	Alkane + alkenes		Alkyl- benzenes		Hexanedioic acid		Pentanedioic acid		Organic Nitrates + nitrites	
	Solvent	Filter	Solvent	Filter	Solvent	Filter	Solvent	Filter	Solvent	Filter
Pasadena	1.4	0.68	0.37	0.38	1.3	1.4	0.79	1.6	0.074	0.39
Pomona	1.8	0.67	0.51	0.41	0.61	1.6	0.48	1.4	---	0.22
Riverside	0.69	0.28	0.26	0.15	0.66	0.88	0.48	0.84	0.02	0.17

a. MSTA for extractable organics obtained by summing results for benzene and methanol-chloroform extracts

b. Results for July 9th episode

2. Recovery of alkylbenzenes from extracts is not significantly different than that observed by direct analysis.
3. Recovery of hexanedioic acid is somewhat reduced by solvent extract while with pentanedioic acid, solvent extraction reduces the recovery by about a factor of two.
4. Recovery of organic nitrates is less than 20% of that obtained by direct analysis of filter samples.
5. Because of the low recoveries of the compounds selected as model secondary organics from benzene plus methanol-chloroform extraction, direct comparison of organics recovered from cyclohexane and these solvents does not provide a useful measure of solvent selectivity.

As a rationale for these observations, loss of organic nitrates and acids may reflect reactions with water and methanol in the solvents. The benzene used was not anhydrous and, as obtained commercially, can be expected to contain significant amounts of water. By comparison the solubility of water in cyclohexane is low, thus reducing the likelihood of such reactions during cyclohexane extractions. Similarly with methanol-chloroform, an appreciable water content is almost inevitable. However, in this case, reactions with water must compete with reactions with methanol. Reactions of organo-nitrates with water lead to alcohols and carboxylic acids. Both carboxylic acids and nitrates could react with methanol to produce esters and/or ethers.

Appendix F describes a study of the reaction of hexanedioic acid and a C_{20} monocarboxylic acid, abietic acid, with methanol-chloroform under conditions simulating those used during extractions. The results indicate the formation of esters. In the case of hexanedioic acid, the resulting ester is sufficiently volatile to be lost during the solvent removal procedure used for carbon determinations.

Under conditions used for MSTA, volatile esters in the methanol-chloroform extract could be lost without analysis, although further study is needed to prove this. The significance of such reactions on both MSTA and MCC determinations are discussed. A 10% positive error in MCC is estimated based upon the carbon introduced by the solvent and an observed loss of only 4% carbon during vacuum treatment of atmospheric MCC samples.

Because of the greatly reduced likelihood of reaction with solvent components during cyclohexane extraction, it appears reasonable to evaluate the selectivity of this solvent by comparing MSTA of cyclohexane extracts with those for the corresponding filter analyses. Table 9 includes this comparison, from which we conclude:

Table 9

COMPARISON OF CYCLOHEXANE SOLUBLE ORGANICS AND DIRECT ANALYSIS OF FILTER SAMPLES BY MSTA ($\mu\text{g}/\text{m}^3$)

Episode	Site	Alkanes + alkenes		Alkyl-benzenes		Hexanedioic acid		Pentanedioic acid		Organic nitrates + nitrites	
		cyc.	filter	cyc.	filter	cyc.	filter	cyc.	filter	cyc.	filter
July 9	Pasadena	1.6	0.76	0.13	0.38	1.0	1.4	0.0	1.6	0.16	0.39
July 9	Pomona	1.3	0.76	0.16	0.41	0.11	1.6	0.05	1.4	0.047	0.22
July 9	Riverside	0.89	0.37	0.13	0.15	0.47	0.88	0.15	0.84	---	0.17
July 10	Pasadena	1.2	0.63	0.16	0.38	1.0	1.8	---	1.3	---	0.17
July 10	Pomona	1.4	0.68	0.09	0.32	0.29	1.1	---	1.4	0.022	0.090
July 10	Riverside	0.60	0.32	0.16	0.20	0.18	1.0	---	0.96	---	0.032

$$\text{Ratio} = \frac{\text{Total secondary organics}^a}{\text{Total primary organics}^b} = \frac{3.4 \text{ (filters)}}{0.56 \text{ (cyclohexene)}}$$

- a. Hexanedioic acid + pentanedioic acid + organic nitrates and nitrites
 b. Alkanes + alkenes + alkylbenzenes

1. Recovery of alkanes plus alkenes is enhanced by solvent extraction (just as with benzene followed by methanol-chloroform).
2. Recovery of the alkylbenzenes is lower than obtained by filter analysis.
3. Recovery of hexandioic acid is, on average, about 40% of that obtained by filter analysis.
4. Recovery of pentanedioic acid is, on average, only a few percent of that obtained by filter analyses.
5. Recovery of organic nitrates range from below detection to 40% of that obtained by filter analysis.

Using as an indicator of cyclohexane's selectivity for primary organics the ratio of the sum of secondary organic indicator compounds to the sum of the primary organic compounds given in Table 9, the cyclohexane extract has, on average, only 1/6 the abundance of secondary organics relative to that in the original filter.

We conclude from this analysis that the MSTA results can be interpreted to support the extraction of primary organics by cyclohexane with high efficiency while secondary organics are extracted with lower efficiency. The lower recoveries of pentanedioic compared to hexanedioic acid are consistent with a decreased solubility in cyclohexane as the ratio of oxygen/carbon increases (i.e., as the proportion of polar to non-polar bonds increases). Although extracted with reduced efficiency, secondary organics are clearly extracted to a significant degree by cyclohexane. If secondary organics predominate in a given sample, the amount of secondary material extracted by cyclohexane might equal or surpass the quantity of primary organics. Accordingly, the extraction by cyclohexane will henceforth be considered to provide an upper limit to the primary organic carbon present. Conversely, the carbon solubilized by benzene plus methanol-chloroform in excess of that extracted by cyclohexane will be considered a lower limit to the secondary organic carbon present.

Conclusions from MSTA results regarding the selectivity of solvent extractions might be weakened by the similar trends observed in extractions with cyclohexane and in benzene plus methanol-chloroform. In the latter case low recoveries of polar organics are interpreted in terms of chemical reactions which are supported by control studies. With cyclohexane, the similar trends are interpreted based on low solubility. The bases for these interpretations appear reasonable and we consider the MSTA data to provide support for the solvent extraction technique.

B. Pyrolysis GC-MS of Pre-Extracted Particulate Samples

Qualitative results have been obtained thusfar for two samples. Both are from the same 14-hour sample collected in Riverside. In one case,

a filter section was pre-extracted with cyclohexane and in the second, with benzene, followed by methanol-chloroform. The resulting spectra obtained from the residual carbonaceous material include a series of hydrocarbons with a few mono-functional oxygenated materials. The spectra indicate that substantially higher organics remained in the sample pre-extracted with cyclohexane relative to the combined solvents. Nevertheless, analyzable levels of organic molecules remain in the samples despite successive extraction with benzene and methanol-chloroform. The extent to which these organics exist in polymeric materials or are merely adsorbed strongly on other substances is still unclear. It is notable that styrene, a likely decomposition product from styrenebutadiene (SBR) rubber, is observed.

VII. Spatial and Diurnal Variations in Particulate Organics

A. Spatial Variations

All filter samples from the July 9 and 10 episodes were analyzed by MSTA to provide a detailed picture of the compounds present on relatively smoggy days at three widely-spaced locations in the SCAB. The complete analytical data are included as Appendix E. As with the extracts, the compounds or classes of compounds selected for discussion were chosen to provide representatives of primary and secondary materials. Total alkanes + alkenes and alkylbenzenes were used as model primary organics while hexanedioic and pentanedioic acids and difunctional organic nitrates + nitrites were used as model secondary organics.

Table 10 compares the MSTA results obtained for the 14-hour samples at the three sites. Of the compounds shown, hexanedioic and pentanedioic acids were the most abundant. The concentrations in Riverside for all constituents listed except alkylbenzenes were lower than at the other sites. In an effort to reduce the influence of atmospheric dilution, concentrations are also expressed relative to those for alkanes + alkenes in the same sample. The two acids exhibit slightly higher relative concentrations at Riverside, a trend also reflected in the ratio of total secondary organics to alkanes + alkenes. Surprisingly, the relative concentration of organic nitrates + nitrites is not higher at Riverside compared to Pasadena. From this table, it is concluded that the 14-hour average organic aerosol at Riverside, collectable on a filter, is generally similar to that obtained in Pasadena and Pomona.

A similar comparison of the three sites employing solvent extraction-carbon analysis* is shown in Table 11, including data for four episodes. Our observations from these results are as follows:

1. The soluble carbon ranges from 49 to 68% of the total carbon at all sites, a significantly lower fraction than observed in the ACHEX. The upper limit estimate of elemental carbon, C_e , is, on average, the most abundant form of carbon at all sites.

*A computer listing of all solvent extraction carbon analyses for 14 and 2 hour samples is included as Appendix G.

Table 10

ANALYSIS OF 14-HOUR FILTER SAMPLES BY MSTA^a

Episode	Site ^b	Total Alkanes + Alkenes		Alkylbenzenes		Hexanedioic Acid		Pentanedioic Acid		Organic Nitrites + Nitrates		Σ Secondary ^c	
		$\mu\text{g}/\text{m}^3$	Relative	$\mu\text{g}/\text{m}^3$	Relative	$\mu\text{g}/\text{m}^3$	Relative	$\mu\text{g}/\text{m}^3$	Relative	$\mu\text{g}/\text{m}^3$	Relative	$\mu\text{g}/\text{m}^3$	Relative
July 9	Pa	0.68	1.0	0.13	0.19	1.4	2.1	1.6	2.4	0.39	0.6	3.4	5.0
July 9	Po	0.67	1.0	0.16	0.24	1.6	2.4	1.4	2.1	0.22	0.3	3.2	4.8
July 9	Riv	0.28	1.0	0.13	0.46	0.88	3.1	0.84	3.0	0.17	0.6	1.9	6.8
July 10	Pa	0.52	1.0	0.16	0.31	1.8	3.5	1.3	2.5	0.17	0.3	3.3	6.3
July 10	Po	0.59	1.0	0.09	0.15	1.1	1.9	1.4	2.4	0.090	0.15	2.6	4.4
July 10	Riv	0.23	1.0	0.16	0.70	1.0	4.4	0.96	4.2	0.032	0.14	2.0	8.7

a. Concentrations given in $\mu\text{g}/\text{m}^3$ and relative to the concentrations of total alkanes + alkenes in the same sample.

b. Pa = Pasadena
Po = Pomona
Riv = Riverside

c. The sum of hexanedioic, pentanedioic acids and organic nitrates + nitrites.

Table 11

COMPOSITION OF 14-HOUR CARBONACEOUS SAMPLES BY
SOLVENT EXTRACTION-CARBON ANALYSIS

(% of Total Carbon)

<u>Episode</u>	<u>Site</u>	<u>Sol. C</u>	<u>C_p</u>	<u>C_s</u>	<u>C_e</u>
B	Pasadena	58.2	17.5	40.7	41.8
	Pomona	54.1	18.5	35.6	45.9
	Riverside	58.5	15.3	43.2	41.5
C	Pasadena	57.8	13.7	44.1	42.2
	Pomona	48.5	16.8	31.7	51.5
	Riverside	58.5	15.3	43.2	41.5
D	Pasadena	67.7	19.9	47.8	32.4
	Pomona	58.6	20.8	37.8	41.4
	Riverside	57.6	15.4	42.2	42.4
E	Pasadena	55.8	20.4	35.4	44.2
	Pomona	50.1	16.5	33.5	50.0
	Riverside	52.8	14.1	38.6	47.2
	Mean	56.5	17.0	39.5	43.5

C_p = Primary organic carbonC_s = Secondary organic carbonC_e = Elemental organic carbon as estimated by insoluble carbonSol. C = C_p + C_s

2. Excepting Episode C, C_p at Riverside is consistently a somewhat smaller fraction of the total carbon than at the other sites.
3. No trends in the composition of C_s with location are evident. On average, the lower limit estimate of secondary organic carbon, C_s , is about twice the upper limit estimate of primary organic carbon, C_p (i.e., the true secondary organic C/primary organic carbon ≥ 2) at all sites.
4. Conclusions from MSTA and solvent extraction-carbon analyses are similar.

B. Diurnal Variations

Selected results employing MSTA for the July 9 and 10 episodes (B and C) are presented first in tabular form so that data for all of the species discussed in the preceding section can be included. In addition, plots of diurnal patterns for the two primary organic indicators (total alkanes + alkenes and alkylbenzenes) and the total secondary organic indicators (hexanedioic acid + pentanedioic acid + organic nitrates and nitrites) will be presented adjacent to corresponding plots obtained by the solvent extraction-carbon analysis technique. It should be noted that the diurnal variations of the secondary organics will be effectively those for the acids since the nitrate + nitrite concentration is relatively small.

Considering the MSTA data compiled in Tables 12-17, the ratio of model secondary (i.e., the sum of hexanedioic and pentanedioic acids and organic nitrates + nitrites) to model primary (total alkanes + alkenes + alkylbenzenes) shown in these tables can be readily interpreted. On both days, the diurnal maximum in this ratio changes in the order Pomona < Pasadena < Riverside. The diurnal maximum in this ratio occurs between 1100 and 1500 hours PDT on July 9 at all sites. On July 10, the morning ratios are substantially elevated over the preceding day but only at Pasadena does the maximum ratio occur during early morning hours. These results are consistent with the carryover of secondary organic aerosols formed on July 9 to the following day. The high early morning concentrations for all constituents on July 10 may reflect both this carryover of aerosols and a low morning mixing height.

Shown for comparison in these tables are the corresponding secondary/primary organics ratios obtained by solvent extraction-carbon analysis. In three of the six cases, the two techniques indicate the same 2-hour period for a diurnal maximum in this ratio with similar diurnal variations. In two other cases, similar trends are observed. The solvent extraction technique also indicates higher morning ratios on July 10 compared to the preceding day.

MSTA results for the likely toluene oxidation products, $C_7H_7NO_3$ and $C_7H_7NO_4$, were examined seeking evidence of diurnal and/or spatial variations. Only 6 of the 24 samples analyzed gave measurable values

Table 12

DIURNAL VARIATIONS OF AEROSOL CONSTITUENTS BY MSTA ($\mu\text{g}/\text{m}^3$)

Pasadena July 9, 1975

Time (PDT)	Total alkanes + alkenes	Alkyl- benzenes	Hexane- dioic acid	Pentane- dioic acid	Organic nitrate + nitrites	Σ Secondary ^a		
						MSTA	$\frac{\Sigma \text{ Secondary}}{\Sigma \text{ Primary}}$	Solvent Ext. ^b
7-9	0.81	0.06	---	---	0.65	0.8		3.3
9-11	1.04	0.37	2.5	1.3	0.12	2.8		4.4
11-13	1.00	0.44	1.6	1.6	---	2.2		3.5
13-15	1.08	0.30	4.8	1.2	1.23	5.2		3.4
15-17	1.01	0.28	2.7	0.97	1.56	4.0		4.7
17-19	0.47	0.07	0.47	0.64	0.48	3.0		5.8
19-21	0.52	0.13	---	2.2	0.36	4.0		5.0
					Mean:	3.1 \pm 1.4		4.3 \pm 1.0

a. The sum of the acids and nitrates + nitrites.

b. MSTA results are the ratio of Σ Secondary to total alkanes + alkenes + alkylbenzenes.
 The solvent extraction results are the ratio of secondary to primary organic carbon obtained by selective solvent extraction and carbon determinations.

Table 13

DIURNAL VARIATIONS OF AEROSOL CONSTITUENTS BY MSTA ($\mu\text{g}/\text{m}^3$)

Pomona, July 9, 1975

Time (PDT)	Total alkanes + alkenes	Alkyl- benzenes	Hexane- dioic acid	Pentane- dioic acid	Organic nitrate + nitrites	Σ Secondary ^a		Σ Secondary ^b	
						MSTA	Σ Primary	MSTA	Solvent Ext.
7-9	0.68	0.30	0.34	0.20	0.10	0.6	0.6	0.6	3.7
9-11	0.87	0.67	1.5	4.1	0.23	3.8	5.8	3.8	1.7
11-13	0.86	0.75	3.5	3.5	0.39	4.6	7.4	4.6	3.5
13-15	0.90	0.54	3.4	4.4	0.17	5.6	8.0	5.6	5.0
15-17	1.13	0.65	4.2	1.8	0.033	3.4	6.0	3.4	4.8
17-19	1.17	0.48	2.9	2.6	0.12	3.4	5.6	3.4	4.3
19-21	1.13	0.51	1.3	2.4	---	2.3	3.7	2.3	4.7
					Mean:	3.4 \pm 1.6	4.0 \pm 1.1		

a. See footnote a, Table 12

b. See footnote b, Table 12

Table 14

DIURNAL VARIATIONS OF AEROSOL CONSTITUENTS BY MSTA ($\mu\text{g}/\text{m}^3$)

Riverside July 9, 1975

Time (PDT)	Total alkanes + alkenes	Alkyl- benzenes	Hexane- dioic acid	Pentane- dioic acid	Organic nitrate + nitrites	Σ Secondary ^a	Σ Secondary ^b	
							MSTA	Σ Primary Solvent Ext.
7-9	0.52	0.26	1.0	0.29	0.08	1.4	2.3	4.3
9-11	0.78	0.39	1.9	1.9	0.15	4.0	3.4	5.3
11-13	0.57	0.30	3.8	3.0	0.16	7.0	8.0	5.4
13-15	1.49	0.60	3.0	2.1	---	5.1	2.4	6.8
15-17	0.66	0.15	1.4	1.7	0.11	3.2	4.0	8.2
17-19	0.63	0.10	1.0	0.96	---	2.0	2.7	5.3
19-21	1.44	0.87	3.4	2.9	0.43	6.7	2.9	5.9
					Mean:		3.7 \pm 2.0	5.9 \pm 1.3

a. See footnote a, Table 12

b. See footnote b, Table 12

Table 15

DIURNAL VARIATIONS OF AEROSOL CONSTITUENTS BY MSTA ($\mu\text{g}/\text{m}^3$)

Pasadena July 10, 1975

Time (PDT)	Total alkanes + alkenes	Alkyl- benzenes	Hexane- dioic acid	Pentane- dioic acid	Organic nitrate + nitrites	Σ Secondary ^a		Σ Secondary ^b	
						MSTA	Σ Primary	MSTA	Solvent Ext.
7-9	0.63	0.22	1.2	2.6	0.36	4.2	4.9	4.9	4.7
9-11	0.73	0.28	2.2	2.0	0.06	4.3	4.3	4.3	9.8
11-13	1.06	0.48	2.9	1.9	0.17	5.0	3.2	3.2	3.3
13-15	1.17	0.64	3.4	2.8	---	6.2	3.4	3.4	3.6
15-17	0.70	0.22	1.3	2.0	---	3.3	3.6	3.6	2.8
17-19	0.69	0.18	1.1	1.5	0.10	2.7	3.1	3.1	2.6
19-21	0.65	0.18	0.94	0.97	0.048	2.0	2.4	2.4	3.1
					Mean:	3.6 \pm .8	4.3 \pm 2.5		

a. See footnote a, Table 12

b. See footnote b, Table 12

Table 16

DIURNAL VARIATIONS OF AEROSOL CONSTITUENTS BY MSTA ($\mu\text{g}/\text{m}^3$)

Pomona July 10, 1975

Time (PDT)	Total alkanes + alkenes	Alkyl- benzenes	Hexane- dioic acid	Pentane- dioic acid	Organic nitrate + nitrites	Σ Secondary ^a		Σ Secondary ^b	
						Σ Secondary	MSTA	Σ Primary	Solvent Ext.
7-9	1.42	1.05	4.3	4.0	0.42	8.7	3.5	2.5	
9-11	1.05	0.72	3.6	4.1	0.29	8.0	4.5	4.8	
11-13	0.88	0.77	1.7	2.0	0.18	3.9	2.4	5.5	
13-15	1.06	0.36	2.0	1.4	0.071	3.5	2.5	3.9	
15-17	1.44	0.79	2.3	3.0	---	5.3	2.4	3.1	
17-19	1.57	0.97	4.7	5.9	0.12	10.7	4.2	3.5	
19-21	1.77	0.58	1.9	0.73	0.16	2.8	1.2	3.2	
					Mean:		3.0 \pm 1.2	3.8 \pm 1.0	

a. See footnote a, Table 12

b. See footnote b, Table 12

Table 17

DIURNAL VARIATIONS OF AEROSOL CONSTITUENTS BY MSTA ($\mu\text{g}/\text{m}^3$)

Riverside July 10, 1975

Time (PDT)	Total alkanes + alkenes	Alkyl- benzenes	Hexane- dioic acid	Pentane- dioic acid	Organic nitrate + nitrites	Σ Secondary ^a		Σ Secondary ^b	
						Σ Primary	MSTA	Σ Primary	Solvent Ext.
7-9	1.37	0.54	5.1	1.2	0.28	6.6	3.5	4.8	
9-11	1.21	0.71	3.0	4.7	0.26	8.0	4.2	5.6	
11-13	0.86	0.25	---	0.75	---	0.8	0.7	6.3	
13-15	0.74	0.25	2.7	2.9	0.16	5.8	5.9	11.0	
15-17	0.46	0.22	0.73	2.4	---	3.1	4.6	6.8	
17-19	0.53	0.27	0.53	1.3	---	1.8	2.3	8.9	
19-21	0.38	0.13	1.3	0.72	0.023	2.0	3.9	5.8	
					Mean:		3.6 \pm 1.7	7.0 \pm 2.2	

a. See footnote a, Table 12

b. See footnote b, Table 12

and these were in the range 0.003 to 0.006 $\mu\text{g}/\text{m}^3$. The lower limit for reliable quantitation of these samples was ca. 0.01 $\mu\text{g}/\text{m}^3$, making detailed evaluation unwise. Nevertheless, it may be stated that the concentrations of these products was about 10^2 lower than for dicarboxylic acids, products likely to be formed from cyclic olefins. Since the reported atmospheric concentrations (as well as gasoline composition) suggest substantially higher concentrations for toluene relative to cyclic olefins, the results imply a relatively low efficiency for aerosol formation from toluene under atmospheric conditions (consistent with smog chamber results). The longer residence time possible for oxidation of pollutants transported east to Riverside (relative to the transport time for pollutants reaching Pasadena and Pomona) appears insufficient to permit buildup of measurable toluene oxidations products in the particle phase.

MSTA results at the three sites were examined for the total of the tentatively identified terpene oxidations products, pinonic acid, norpinic acid, pinic acid, $\text{C}_9\text{H}_{14}\text{O}_2$, $\text{C}_{10}\text{H}_{14}\text{O}_3$, $\text{C}_{10}\text{H}_{16}\text{O}_2$, and $\text{C}_{10}\text{H}_{16}\text{O}_3$. The range in concentrations observed at the three sites was 0.03 to 0.47 $\mu\text{g}/\text{m}^3$ for individual compounds with somewhat higher values at Pomona compared to the other sites. However, the lower limit for reliable quantitation was here from 0.2 to 0.8 with 85% of the observed values below their corresponding lower limits. The total terpene products represented generally < 10% of the sum of just the more important secondary organic species. Thus, the present data, consistent with those previously discussed for West Covina samples (Section II B), suggests that natural aerosols are minor contributors to the secondary organic aerosol collectable on a hi-vol filter.

The results from the solvent extraction-carbon analysis technique for two-hour samples for July 9-12 (Episodes B-E) are presented as a series of diurnal plots showing primary, secondary, elemental and total carbon, lead and Br/Pb ratio as well as ozone concentrations. These are compared to results for model primary and secondary organics by MSTA. The figures are arranged by episode with the sequence Pasadena, Pomona, Riverside (i.e., from west to east). To aid in later data interpretation, comments are included by episode.

Bromine to lead ratios were used here as an indicator of average aerosol age on the presumption that motor vehicle exhaust is the dominant source of both pollutants. Fresh automotive aerosol exhibits a Br/Pb ratio close to the theoretical value 0.39 while, as the result of volatilization, photolysis and/or other reactions, the Br/Pb ratio can diminish to ca. 0.05 over a period of several hours, remaining approximately constant thereafter.²⁹ In examining the diurnal patterns, it will be noted that secondary organic carbon (C_s) typically is ≥ 3 times the primary organic carbon (C_p). As previously noted, the C_s values are minimum estimates of the true C_s , and C_p , a maximum estimate. Because of the predominance of C_s and the partial inclusion of secondary organics in C_p , the true diurnal variation of C_p may be obscured.

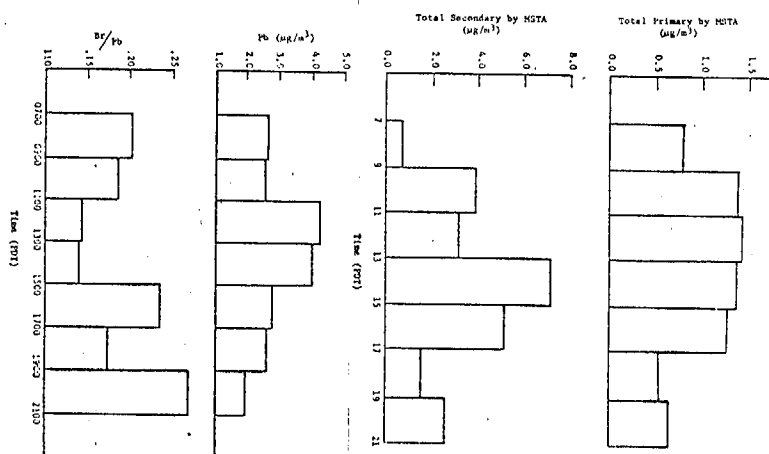
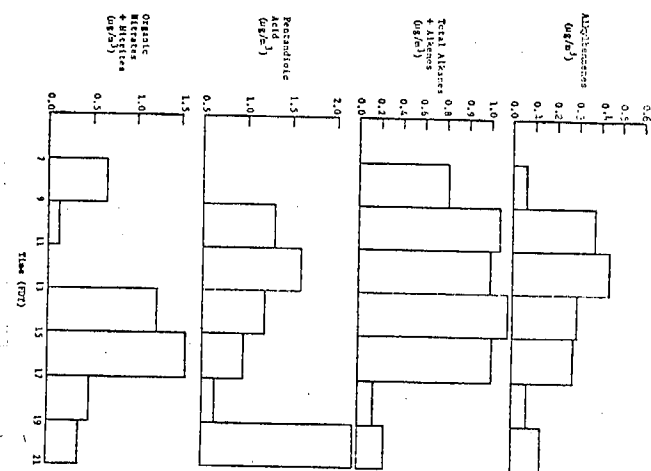
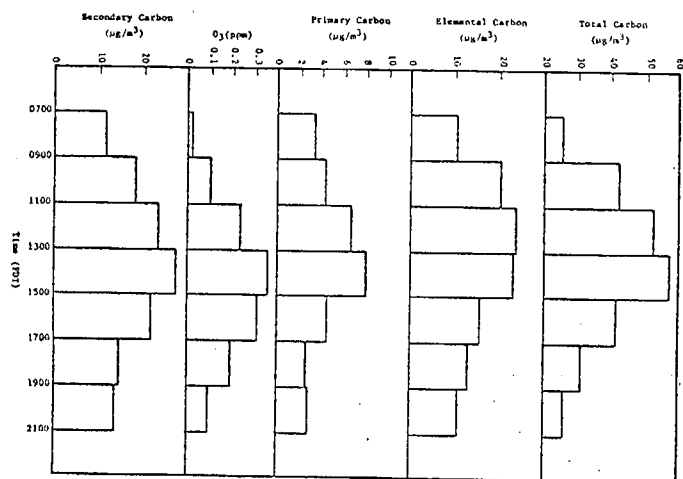
1. Episode B

a. Pasadena (Figure 13)

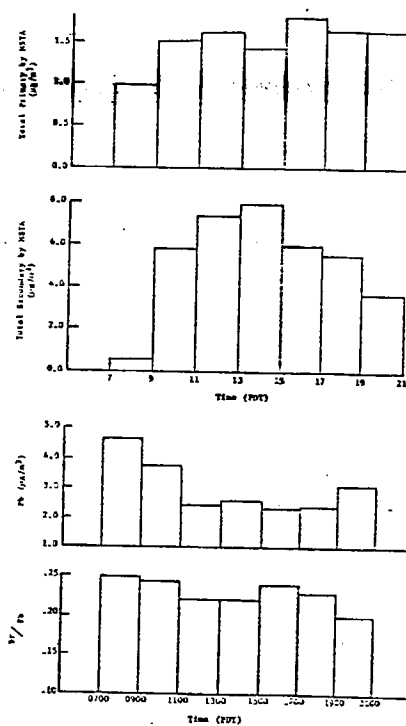
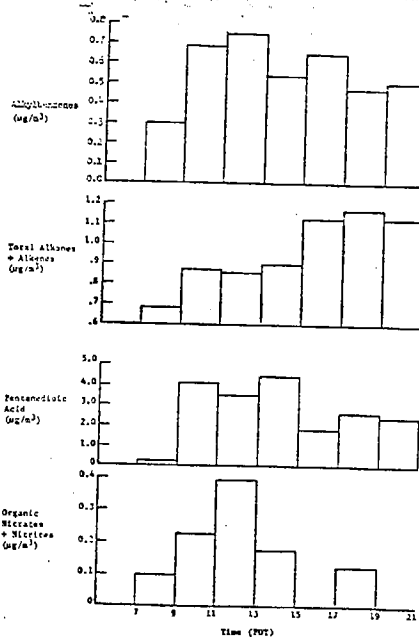
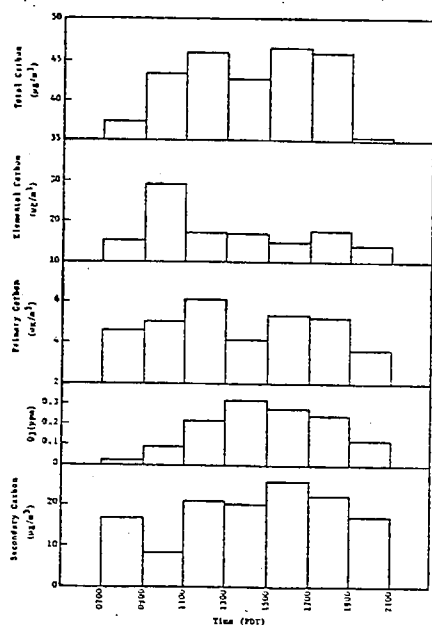
- (1) Two-hour average ozone reached 0.36 ppm indicating rather heavy photochemical smog.
- (2) A morning traffic peak is not seen for primary organic carbon (C_p), elemental carbon or lead. The alkylbenzenes do exhibit a mid-morning maximum more consistent with expectations for a vehicular traffic-related product. However, there is not a good correlation between the patterns for Pb and alkylbenzenes.
- (3) The diurnal variation for all carbonaceous fractions by solvent extraction as well as lead parallel that for ozone with a midday peak (usually 1300-1500).
- (4) The Br/Pb ratio is low during the midday. This plus the high Pb concentrations during this period, suggests the influx of a relatively aged aerosol.
- (5) Total alkanes + alkenes and the two secondary organics by MSTA show similar variations to C_p and C_s excepting the evening peak in pentanedioic acid.
- (6) Total secondary organic indicators and total primary organic indicators by MSTA show similar diurnal patterns with midday maxima.

b. Pomona (Figure 14)

- (1) O_3 reached a 2-hour maximum of 0.32 ppm during the same period as found at Pasadena.
- (2) Elemental carbon (C_e) and C_p show differing diurnal patterns from both O_3 and C_s .
- (3) The diurnal pattern for C_s is generally similar to that for ozone with a maximum displaced later in the day by two hours. A second early morning maximum in C_s is seen.
- (4) The diurnal pattern for lead reveals an early morning maximum and differs substantially from the pattern for both C_p and C_e . The Br/Pb ratio is relatively constant throughout the day and indicates only moderate aging.
- (5) Total alkanes + alkenes and the two secondary organics by MSTA do not correlate well with either C_s or C_p . Alkylbenzenes, however, correlate rather well with C_p but poorly with Pb. The secondary organics by MSTA both show midday



PASADENA
JULY 9, 1975
(Episode B)
Figure 13
- 46 -



PCMOHA
JULY 9, 1975
(Episode B)

Figure 14

- maxima in contrast to total alkanes + alkenes. Total primary organic indicators displays a diurnal pattern similar to that for C_p while total secondary organic indicators resembles the patterns for ozone and C_s .

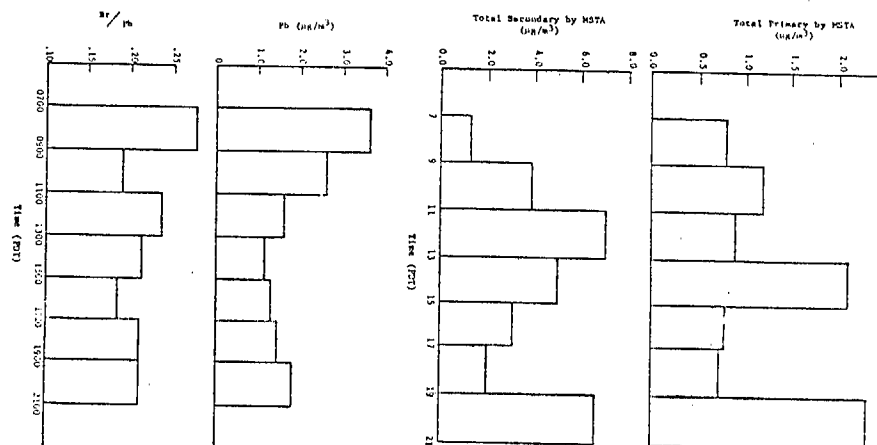
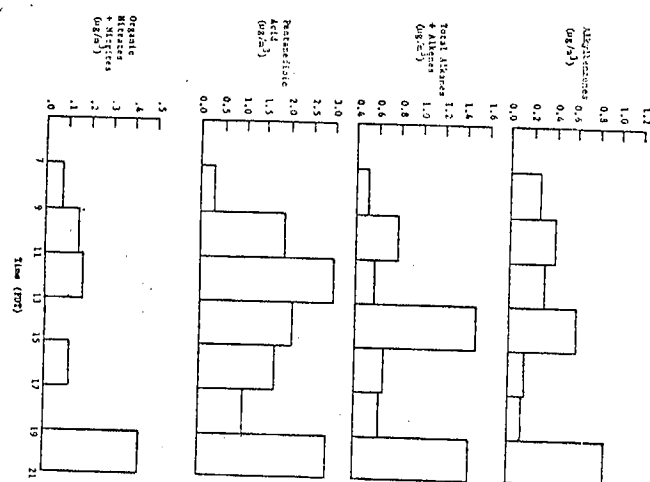
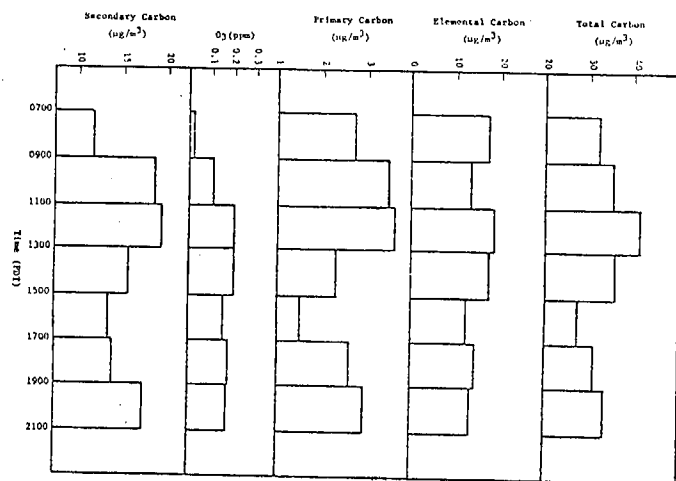
c. Riverside (Figure 15)

- (1) The diurnal pattern of ozone is remarkably flat with values between .17 and .21 ppm over a 10-hour period.
- (2) The diurnal variations of C_e and C_p differ. The latter resembles that for C_s and both are different from the ozone pattern.
- (3) The diurnal pattern for Pb, as in Pomona, exhibits an early morning peak and differs from that of the other pollutants shown. The Br/Pb ratio is maximum at the morning Pb peak.
- (4) Total alkanes + alkenes as well as total primary organic indicators do not correlate well with C_p . Total secondary organic indicators resembles both C_p and C_s in diurnal pattern. Alkylbenzenes correlate well with alkanes + alkenes but poorly with Pb.

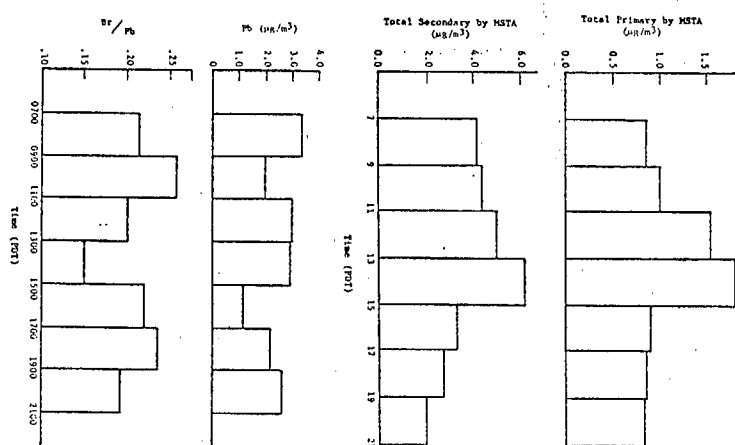
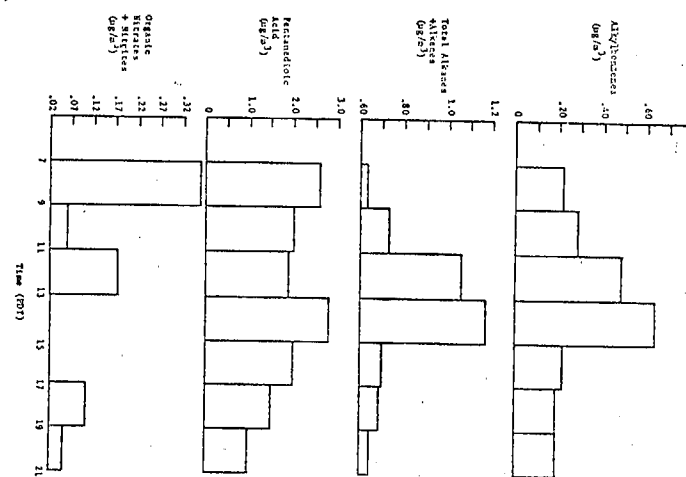
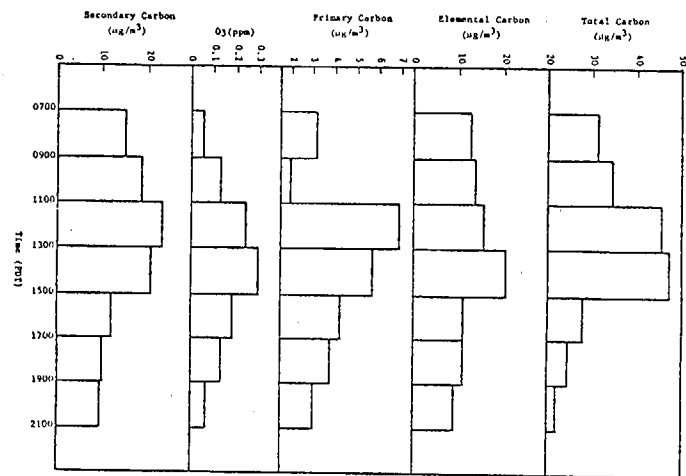
2. Episode C

a. Pasadena (Figure 16)

- (1) The ozone maximum exceeded 0.3 ppm with a typical afternoon maximum.
- (2) The early morning C_s was greater than that experienced on the preceding day. The diurnal maximum in C_s preceded the ozone maximum in contrast to the preceding day.
- (3) No substantial differences existed in the diurnal variations of C_p , C_s and C_e . All differ from the pattern for Pb.
- (4) The diurnal variations by MSTC indicate midday maxima for the two primary organics and total primary organic indicators, similar to C_p and C_s , but an early morning maximum for organic nitrates + nitrites. Total secondary organic indicators show a maximum coincident with O_3 but clearly show elevated morning levels. Alkylbenzenes correlate well with alkanes + alkenes but do not correlate with Pb.
- (5) The Br/Pb ratio suggests the aerosol sampled during the early morning was moderately aged.



RIVERSIDE
JULY 9, 1975
(Episode 3)
Figure 15



PASADENA
JULY 10, 1975
(Episode C)
Figure 16

b. Pomona (Figure 17)

- (1) The O₃ maximum reached 0.26 ppm during the same time period as at Pasadena.
- (2) The early morning C_p, C_s and C_e were substantially greater than on the preceding day.
- (3) The diurnal variation of C_p and C_e differed substantially from that for C_s which, in turn, did roughly parallel the ozone pattern.
- (4) The diurnal pattern for Pb is about the same as those for both C_p and C_e but different than that for C_s.
- (5) The Br/Pb ratio suggests that the air mass sampled during the morning is relatively aged. The high evening ratio is improbable and suggests analytical error.
- (6) Total alkanes + alkenes, while showing an early morning maximum similar to C_p, reveals an afternoon rise and evening maximum not seen for either C_p or C_s. Alkylbenzenes are similar to alkanes plus alkenes but different from Pb. The total secondary organic indicators by MSTA correlates better with C_p than C_s. However, MSTA confirms that both primary and secondary organics have early morning maxima.

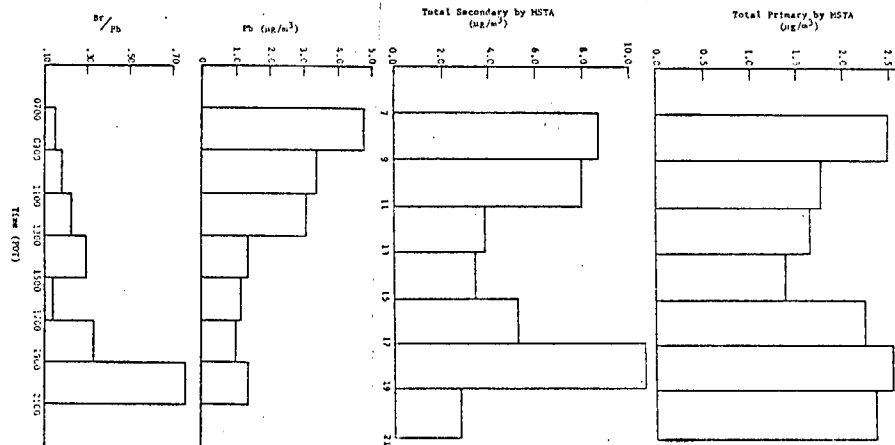
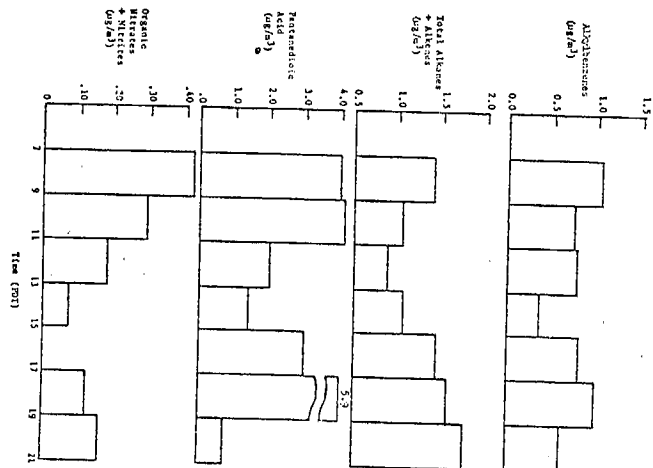
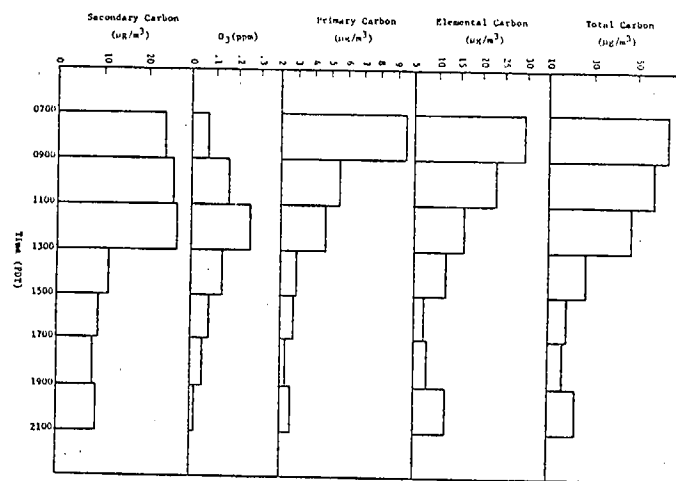
c. Riverside (Figure 18)

- (1) Ozone shows a more typical diurnal variation on this day, compared to that preceding, with a maximum of about 0.19 ppm.
- (2) The diurnal variation of C_p, C_s, C_e and Pb are generally similar with morning maxima.
- (3) The Br/Pb ratio suggests that the air mass sampled during the morning is relatively aged.
- (4) Total primary organic indicators parallel C_p somewhat better than C_s. Total secondary organic indicators by MSTA follows C_s somewhat better than C_p. MSTA confirms that both primary and secondary organics have morning maxima. Alkylbenzenes indicate a mid-morning maximum not seen in C_p and some resemblance to the diurnal pattern for Pb. As in Episode B, pentanedioic acid and alkylbenzenes shown pronounced maxima at the same time. This was only observed in Riverside.

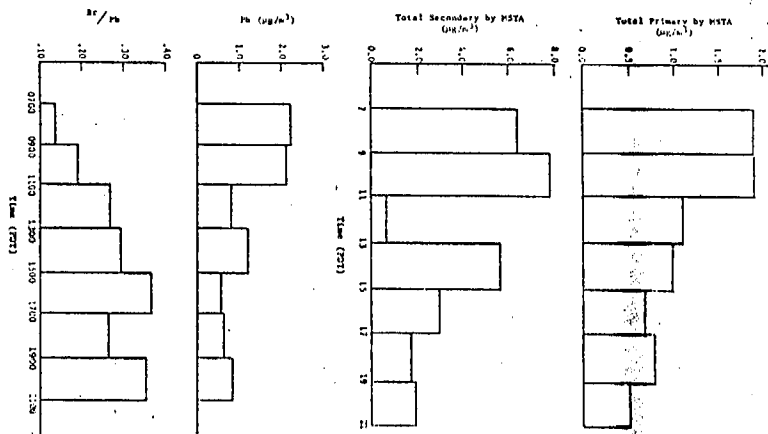
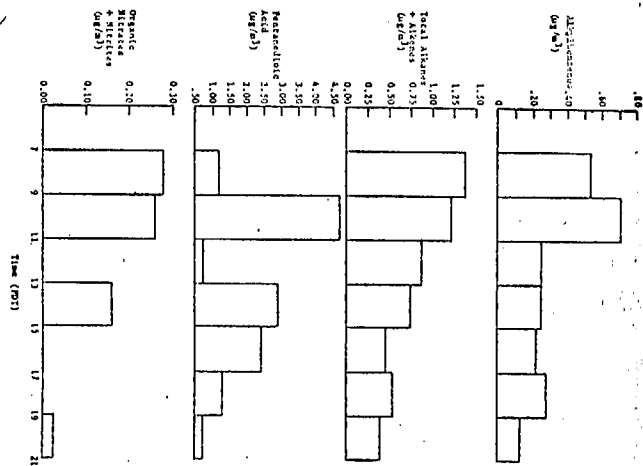
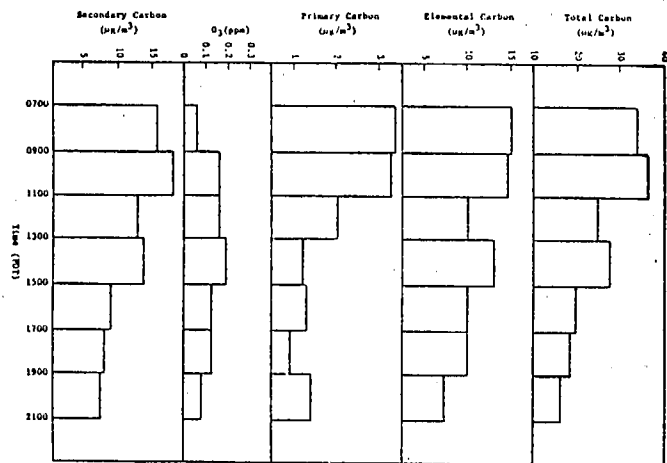
3. Episode D

a. Pasadena (Figure 19)

- (1) The diurnal maximum O₃ concentration reached 0.28 ppm indicating moderate smog.

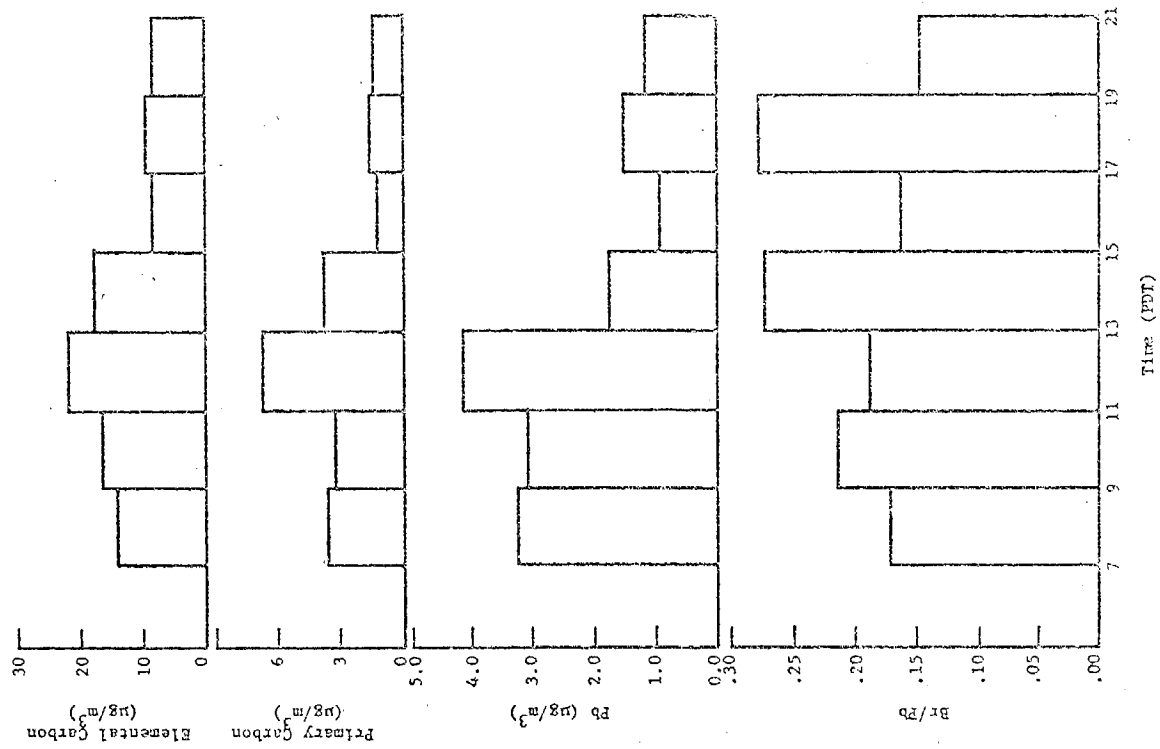
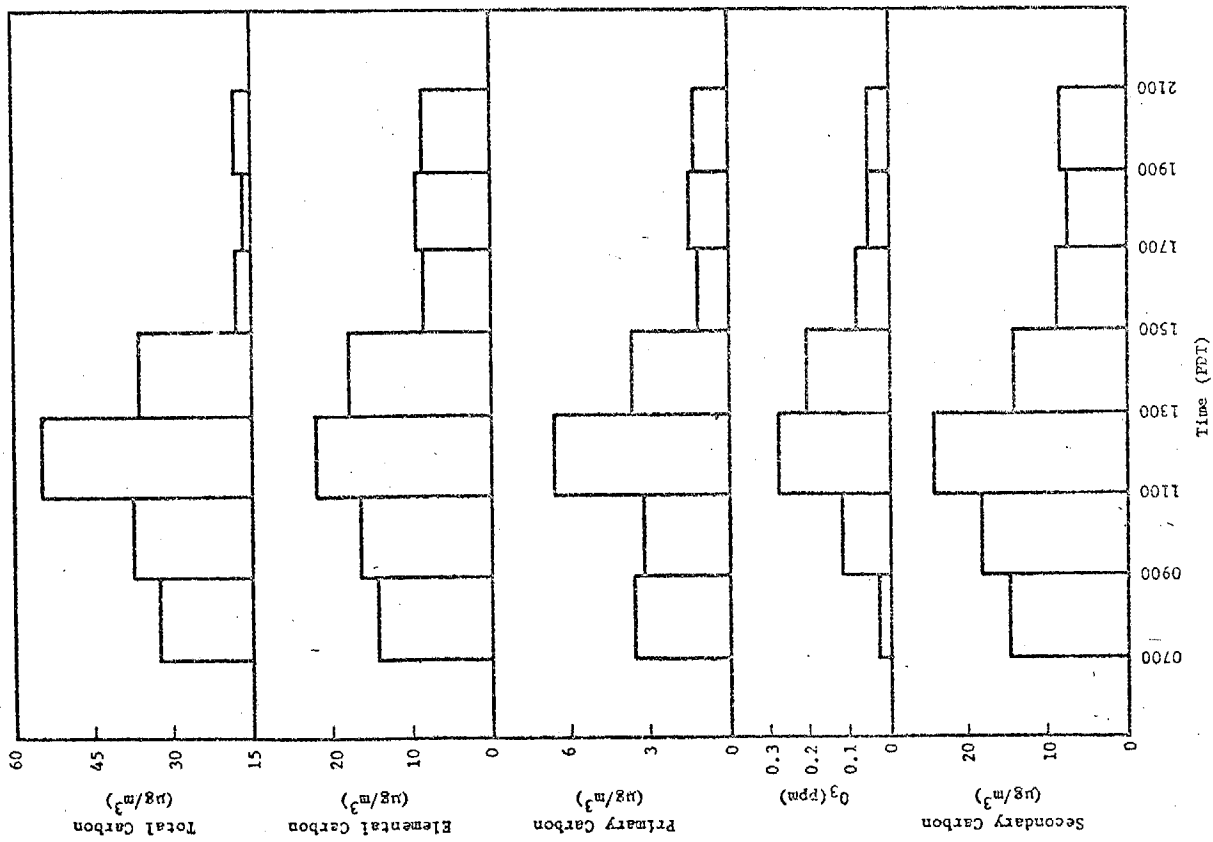


PERKOLA
JULY 10, 1975
(Episode C)
Figure 17



REVERSE
JULY 10, 1975
(Episode C)

Figure 18



PASADENA
JULY 11, 1975
(Episode D)

Figure 19

- (2) The diurnal variations of C_p , C_s , C_e and total C all resembled that for O_3 .
- (3) The early morning concentrations of C_p , C_s and C_e resemble those for Episodes C.
- (4) The Br/Pb ratio suggests that the air mass sampled during the morning is moderately aged.

b. Pomona (Figure 20)

- (1) The diurnal maximum O_3 concentration reached 0.35 ppm but follows by two hours the maximum in Pasadena.
- (2) The early morning C_s is again high and the diurnal maximum in C_s again precedes the ozone peak.
- (3) C_p and C_e show similar diurnal variations with morning maxima but different than that for C_s .
- (4) The Br/Pb ratio is at a minimum in the early morning consistent with the sampling of relatively aged smog. The diurnal maximum of Pb and C_p occur during the same period.

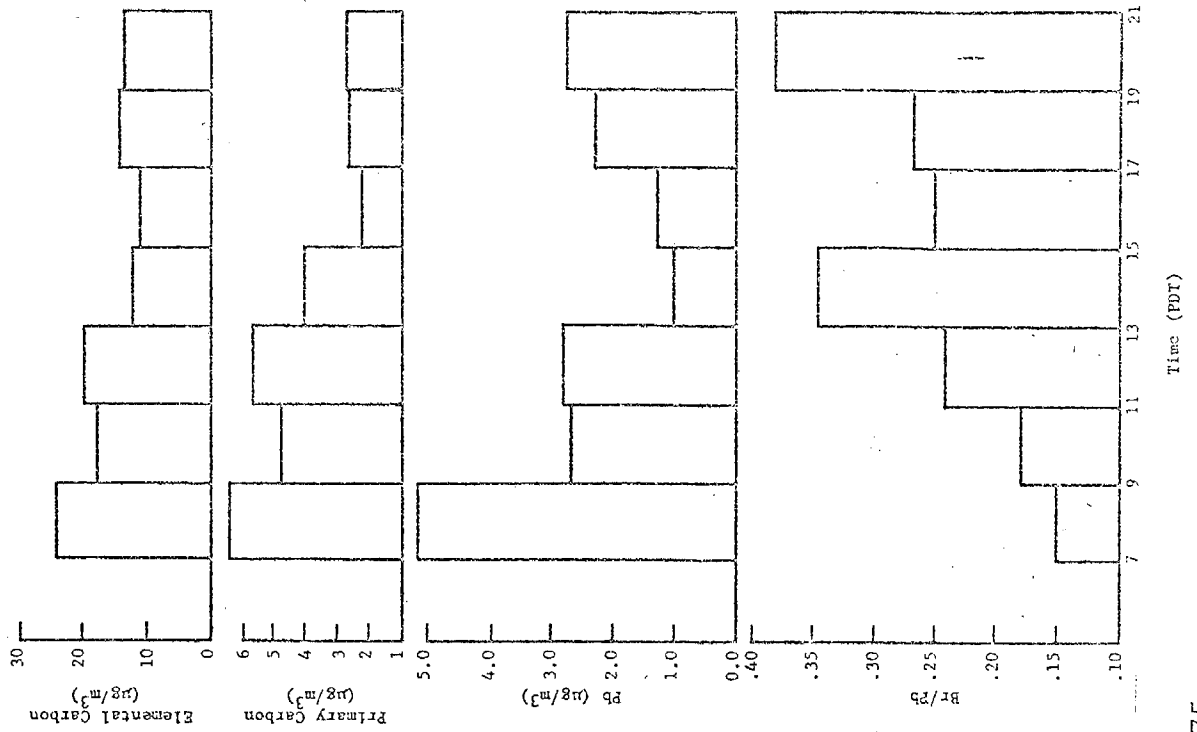
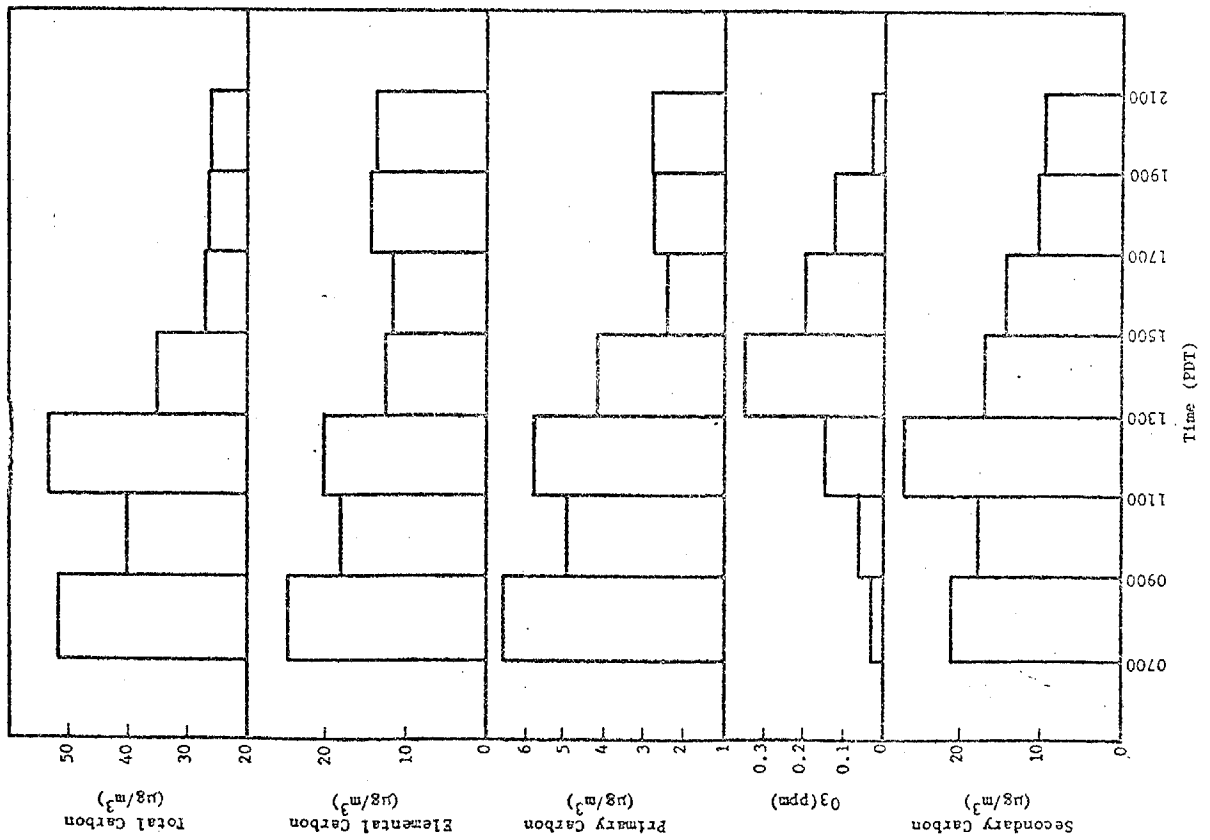
c. Riverside (Figure 21)

- (1) The diurnal maximum for ozone was 0.22 ppm at 1500-1700 hours, the latest period for the ozone maximum experienced for the three episodes discussed thusfar.
- (2) The diurnal pattern for C_s was fairly flat throughout the day with a single maximum coinciding with the O_3 peak. The morning C_s was substantially lower than on the preceding day.
- (3) The diurnal variation for C_p showed a morning maximum while that for C_e was generally flat.
- (4) The Br/Pb ratio shows high morning values indicating relatively fresh aerosol was being sampled.

4. Episode E

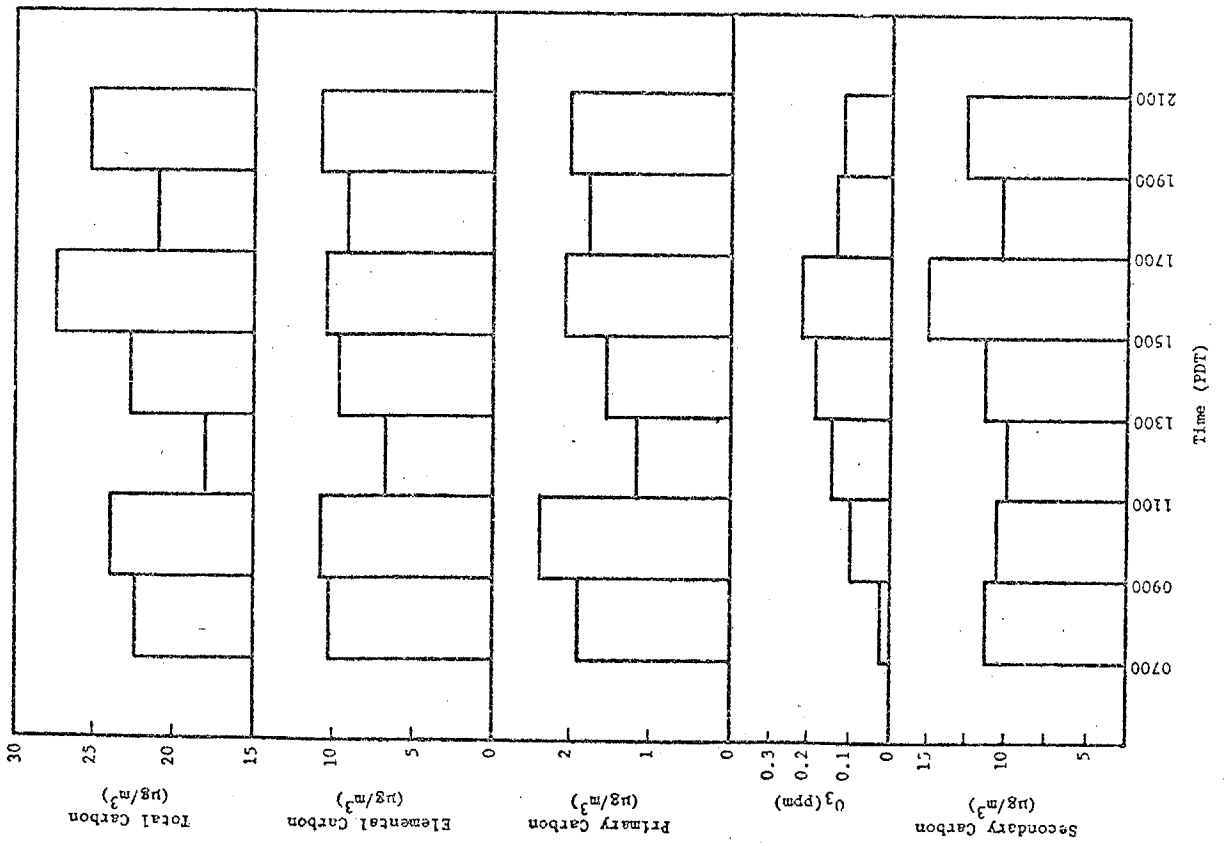
a. Pasadena (Figure 22)

- (1) The O_3 maximum was 0.13 ppm indicating only light smog.
- (2) The early morning levels of C_p , C_s and C_e were much lower than on the preceding days.
- (3) The diurnal variations of C_s coincided with that for O_3 . The peak C_p and C_e also occurred during midday and followed by two hours the O_3 maximum.



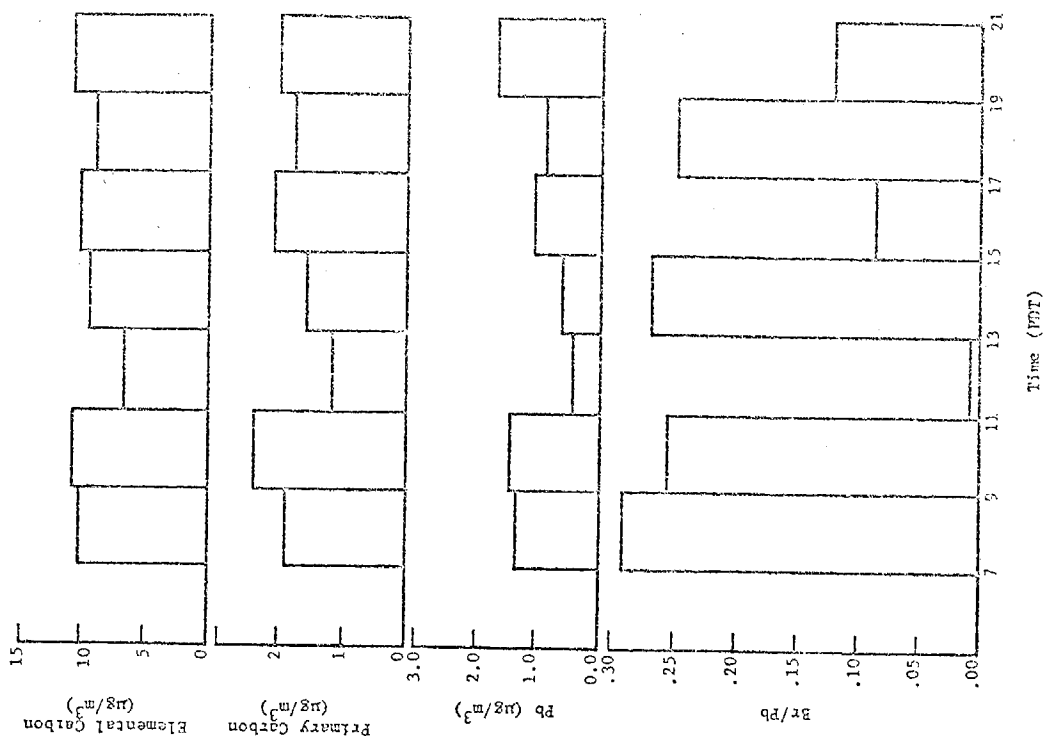
POMONA
JULY 11, 1975
(Episode D)

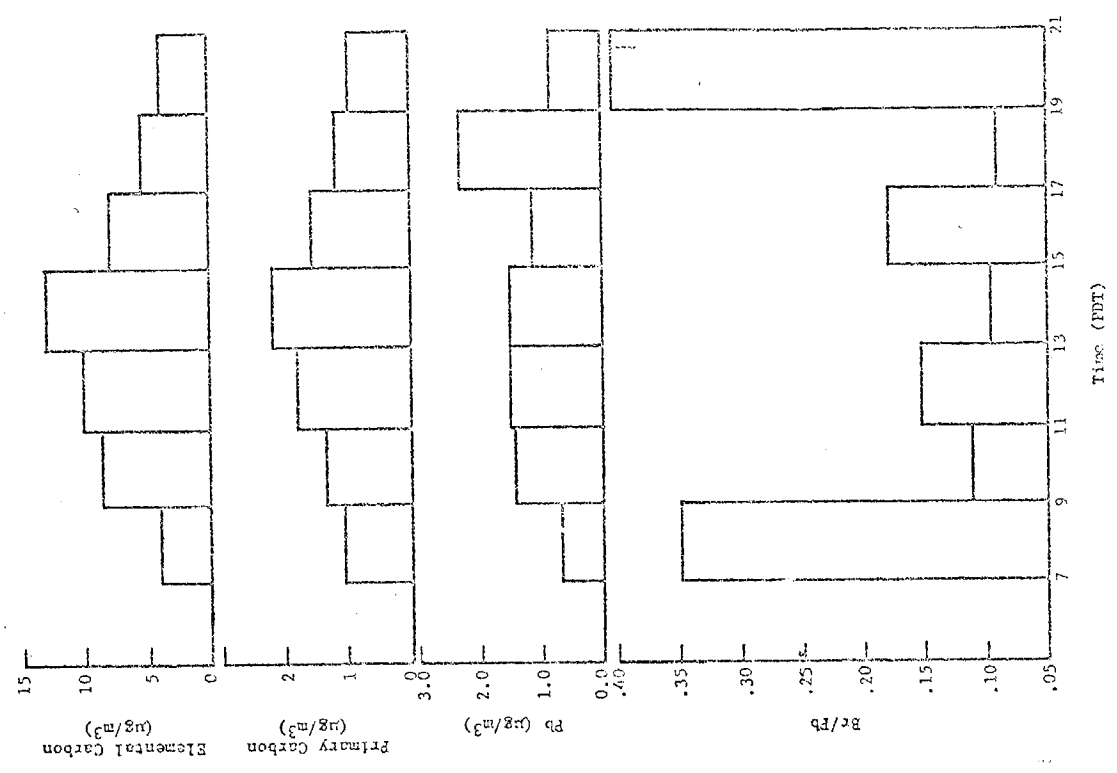
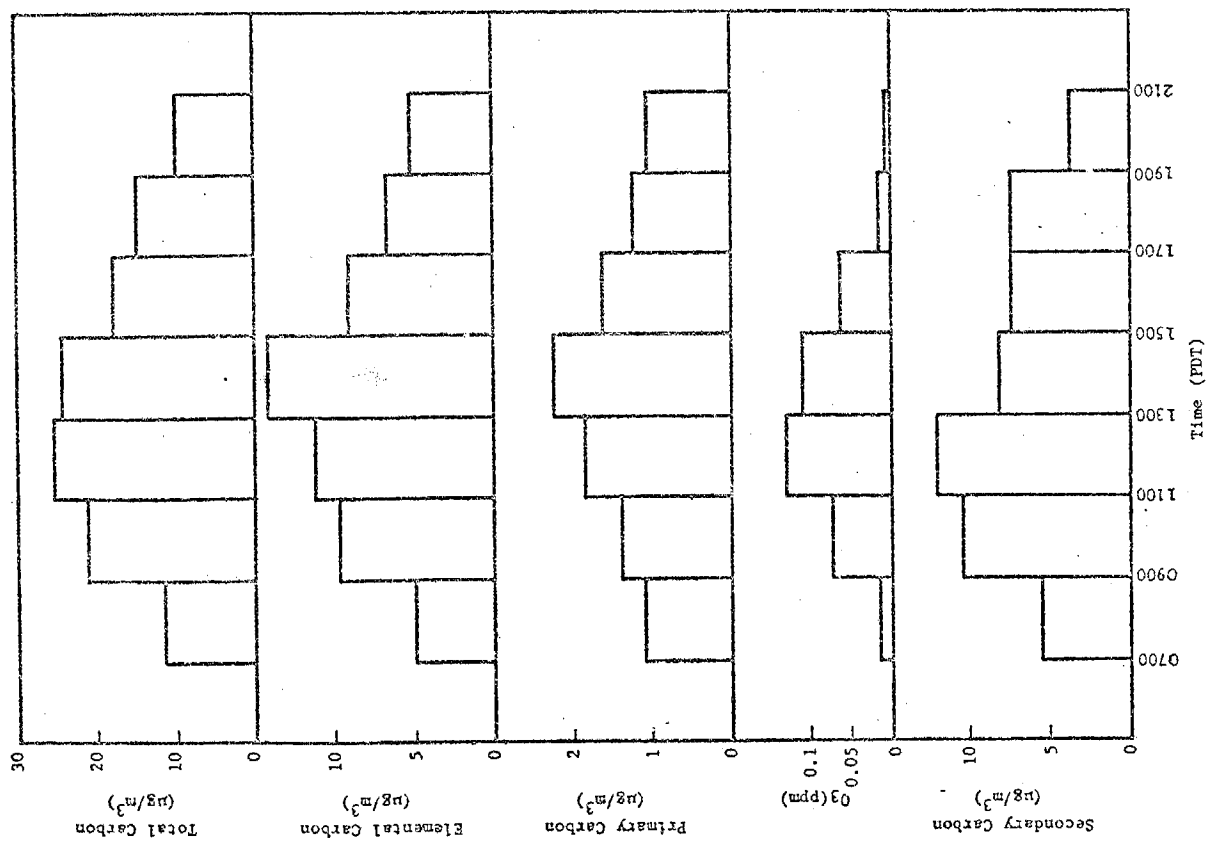
Figure 20



RIVERSIDE
JULY 11, 1975
(Episode D)

Figure 21





PASADENA
JULY 12, 1975
(Episode E)

Figure 22

- (4) Br/Pb ratios are highest in the early morning and evening indicating fresh aerosol is being sampled during these periods.

b. Pomona (Figure 23)

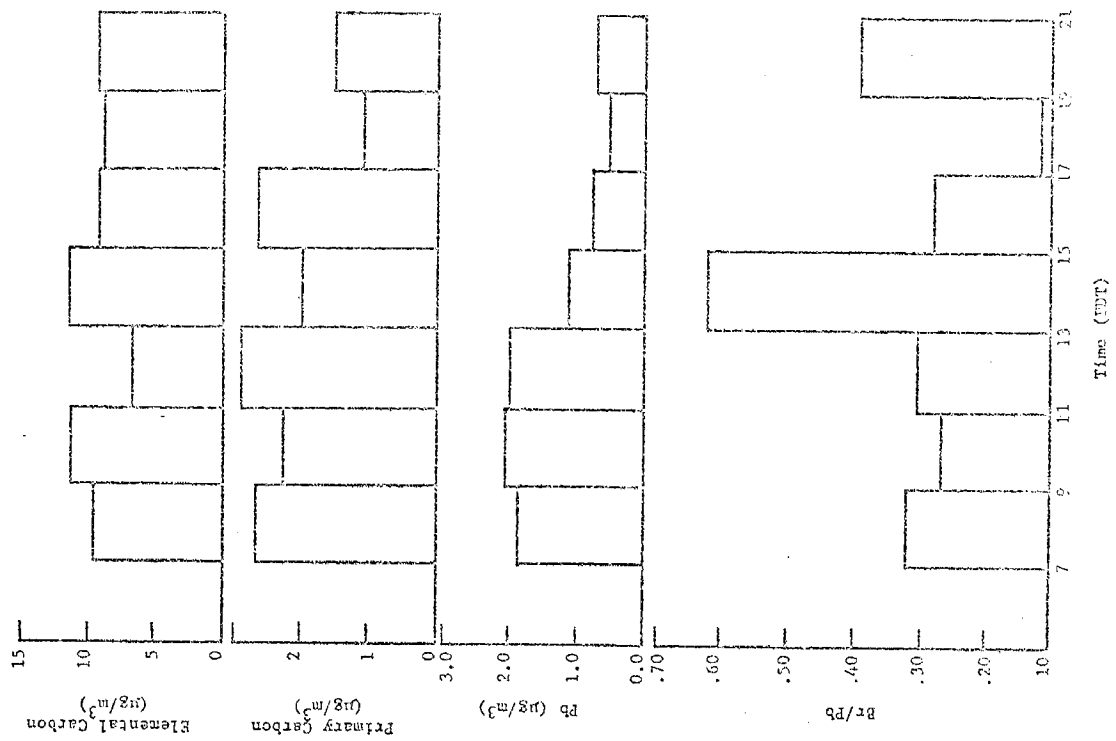
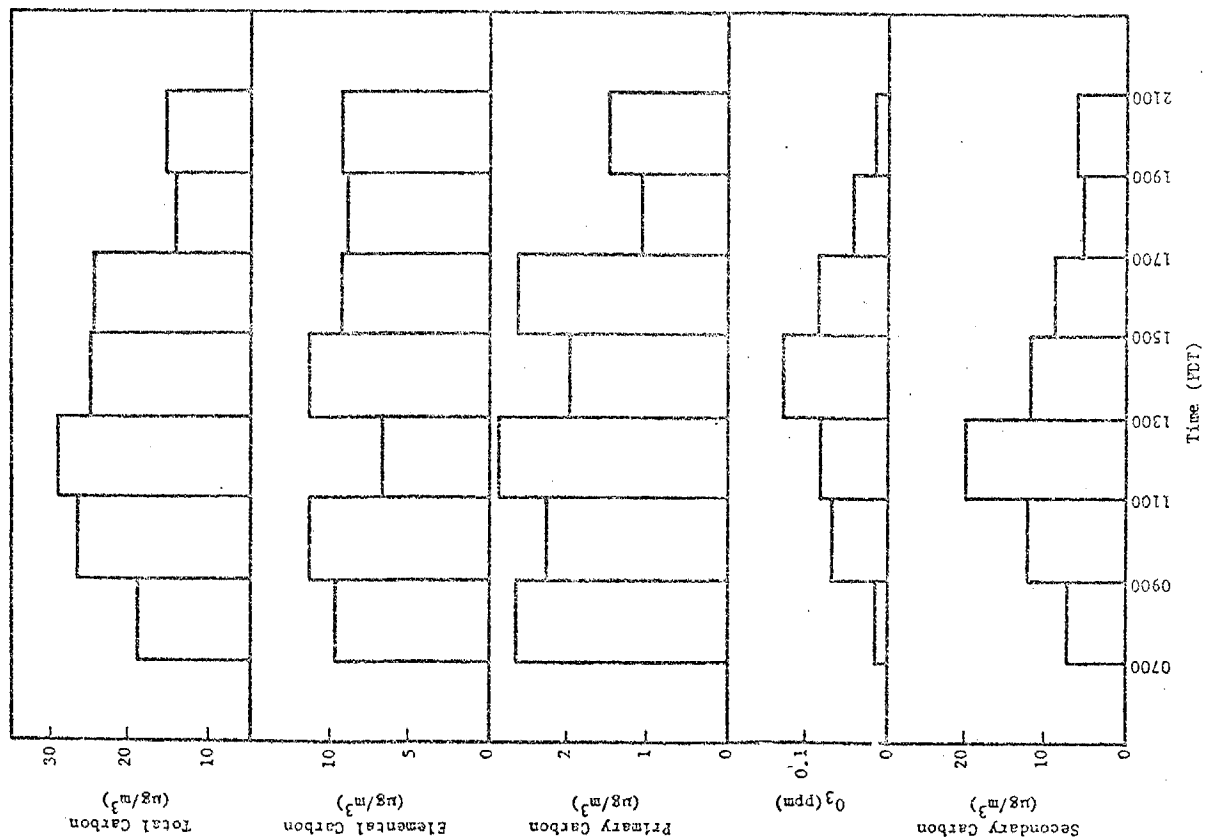
- (1) The O_3 concentration reached 0.13 ppm but followed by two hours the peak in Pasadena.
- (2) The diurnal variation for C_p , C_s and C_e are quite different. The pattern for C_s is similar to that for O_3 but with a peak two hours earlier.
- (3) The Br/Pb ratio indicates relatively fresh aerosol is being sampled during the morning period. The value 0.62 is of questionable validity.

c. Riverside (Figure 24)

- (1) The O_3 concentration reached 0.13 ppm with a broad maximum between 1100 and 1500 hours.
- (2) The diurnal variations of C_p , C_s and C_e were different. The C_p exhibited a sharp early morning maximum. The diurnal maximum for C_p also occurred in the morning. A relatively low Br/Pb ratio is observed during the 7-9 period indicating an aged aerosol during the period preceding the diurnal C_s maximum.

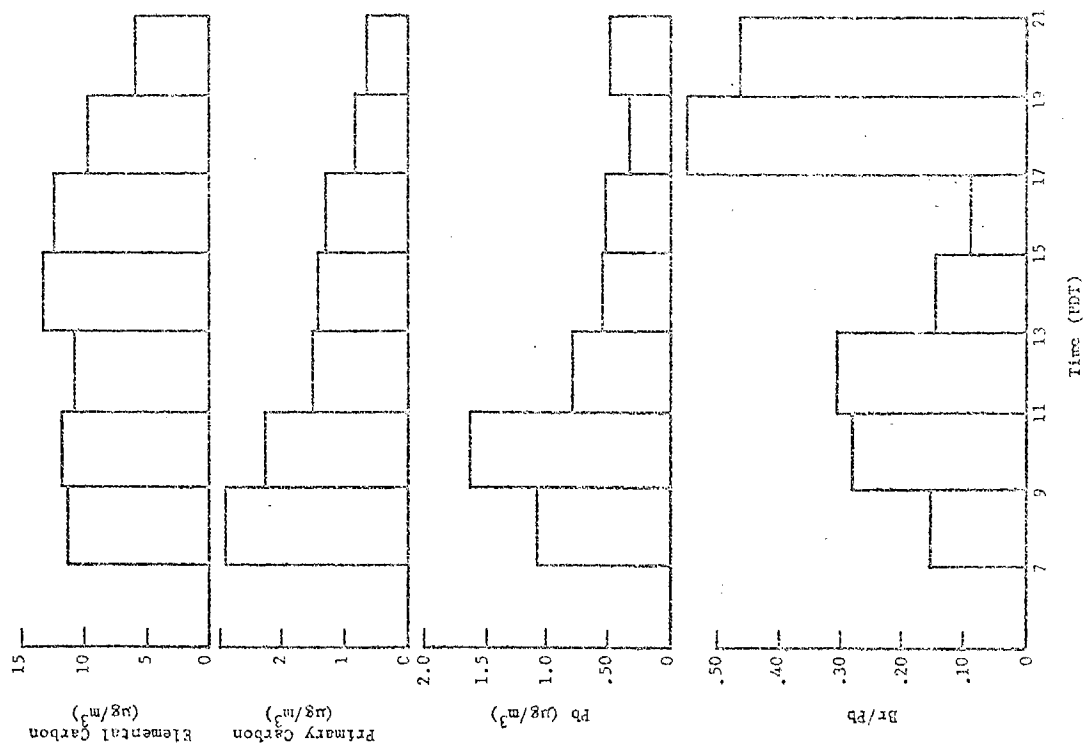
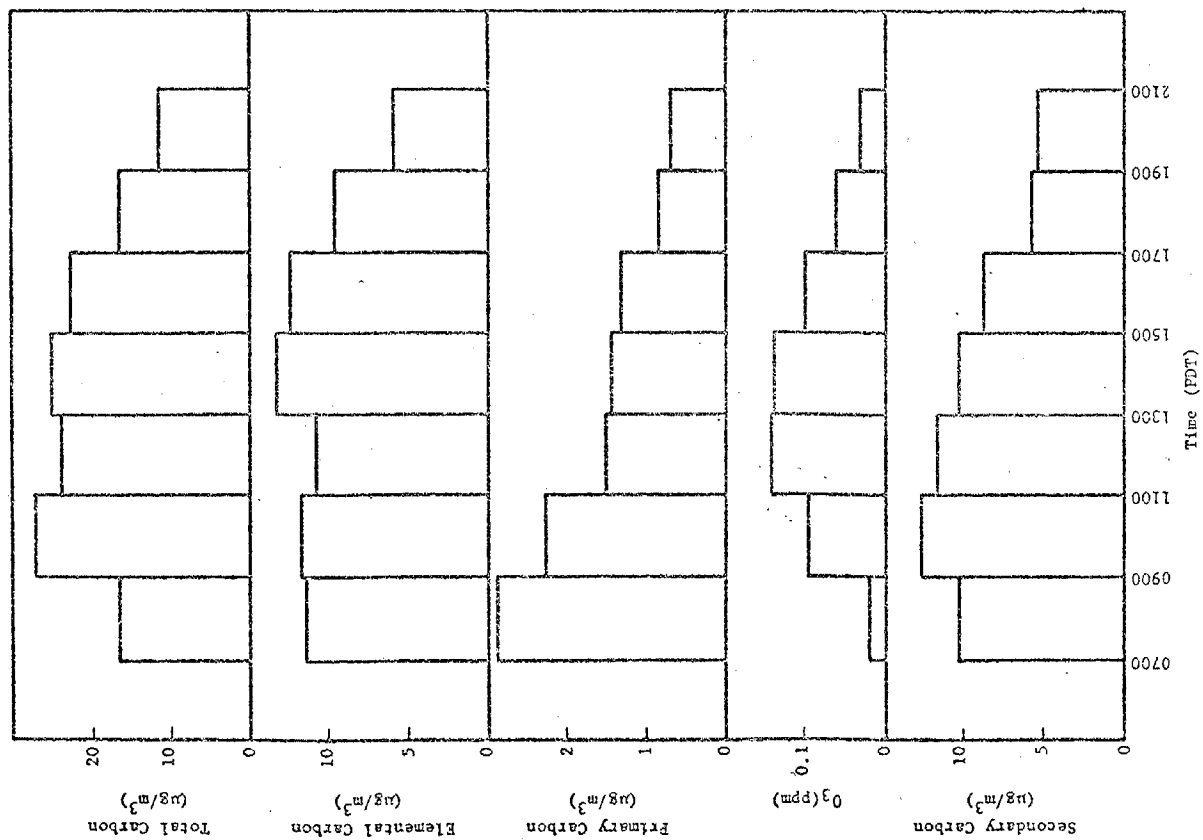
5. Summary of Diurnal Data

- a. Pasadena -- in spite of moderate to heavy smog, the diurnal variations of C_p , C_s , C_e and ozone were generally similar with mid-day maxima. For the second and third day of a four-day sampling period, evidence of carryover of organic aerosols from the preceding day was obtained; Br/Pb ratios were low for morning samples and for Episode C, the MSTA results indicated early morning maxima for some secondary organic compounds. Alkylbenzenes and total alkanes + alkenes generally revealed similar diurnal patterns but the correlation between these organics and Pb was not good.
- b. Pomona -- O_3 maxima were similar in magnitude and time to those at Pasadena. The diurnal variations of C_s were distinct from those for C_p and C_e . For the sequence of Episodes B, C, D and E the diurnal maximum in C_s shifts gradually from following the O_3 maximum by two hours to preceding it by two hours. This trend parallels other indicators of the sampling of aerosol from preceding days: Br/Pb ratios for Episodes C and D are low in contrast to Episode B. However, for Episode E, the morning Br/Pb ratio is relatively high.



POMONA
JULY 12, 1975
(Episode E)

Figure 23



RIVERSIDE
JULY 12, 1975
(Episode E)

Figure 24

- c. Riverside -- ozone levels were lower than at the other sites. As with Pomona and Pasadena, relatively aged aerosol was sampled in the morning on Episode C as indicated by a low Br/Pb ratio, a morning peak in C_s and high concentrations of secondary organics by MSTA. In contrast to Pomona and Pasadena, this was not the case for Episode D. For Episode E, a relatively low Br/Pb ratio (indicating an aged aerosol) in the morning was again accompanied by a diurnal maximum in C_s which preceded the O_3 maximum.

C. Conclusions

The period July 9-11, 1975 appears to be one of stagnation with a buildup of pollutants followed by ventilation and, therefore, fresh aerosol being sampled on July 12. As indicators of such stagnation, we have used low morning Br/Pb ratios, elevated morning secondary organics on July 10 and 11, and diurnal maxima in secondary organics which preceded the daily O_3 peak. The northwesterly wind flow in the morning of July 12, in contrast to the north to northeast pattern observed on the preceding three days, may be a factor in the introduction of cleaner air.

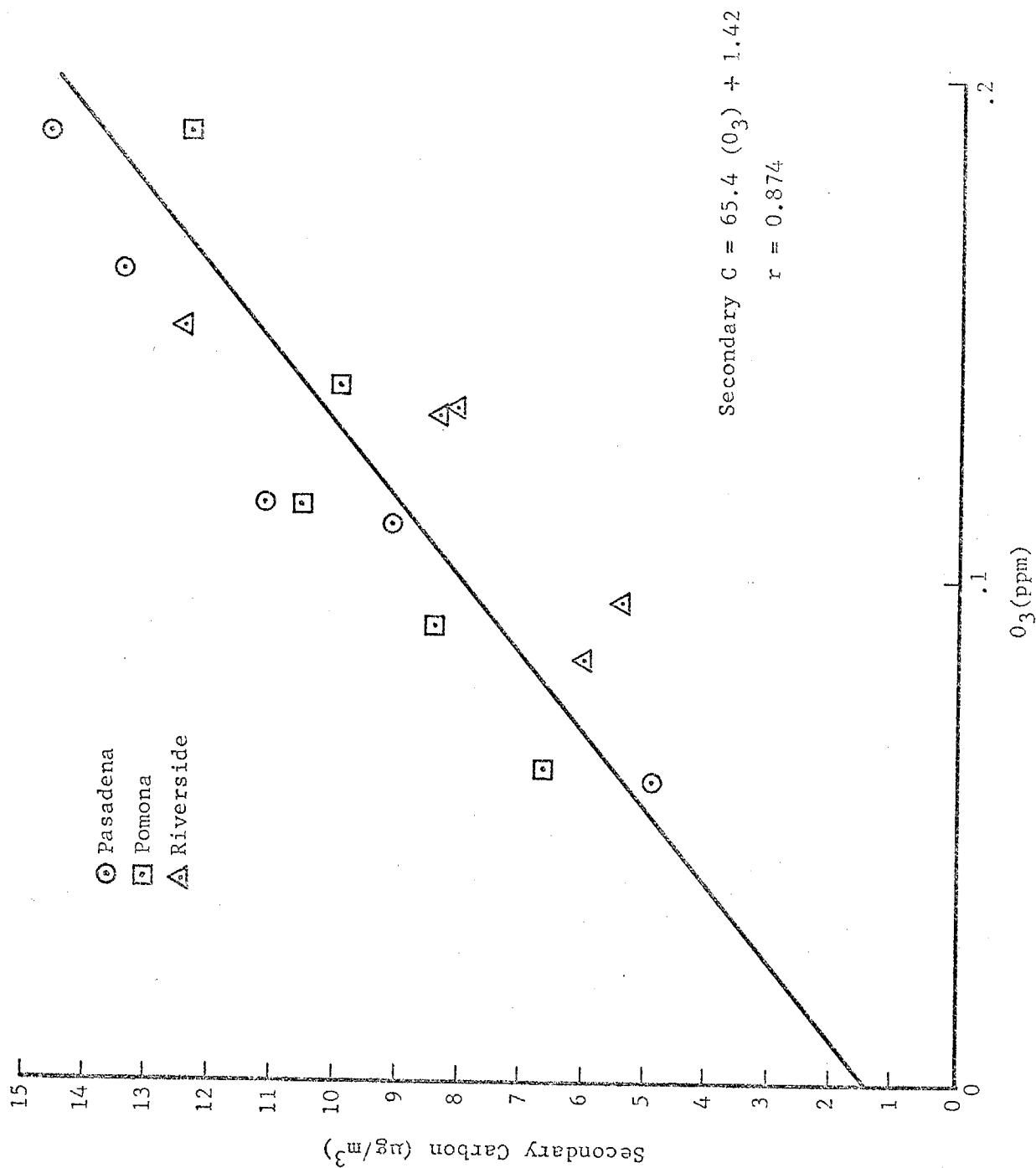
For this period, the composition of the particulate carbonaceous material at Pasadena, Pomona and Riverside was generally similar. Secondary organic carbon, C_s , generally exceeded primary organic carbon, C_p , by a factor ≥ 2 . Elemental carbon, C_e , was, on average, the most abundant carbon form. There was no clear indication that a particular type or class of secondary organics contributes proportionately more to these materials at any of the three sites.

The secondary organics identified by MSTA correspond to products expected from cyclic alkenes and open-chain dienes. The oxidation products associated with toluene, the most abundant aromatic hydrocarbon observed in ambient air, and terpenes, naturally emitted reactive alkenes, were two orders of magnitude lower in concentration suggesting relatively little contribution from such precursors throughout the Basin.

In cases where similar diurnal variations were observed for C_p and C_s , MSTA results for model primary and model secondary products usually showed analogous behavior.

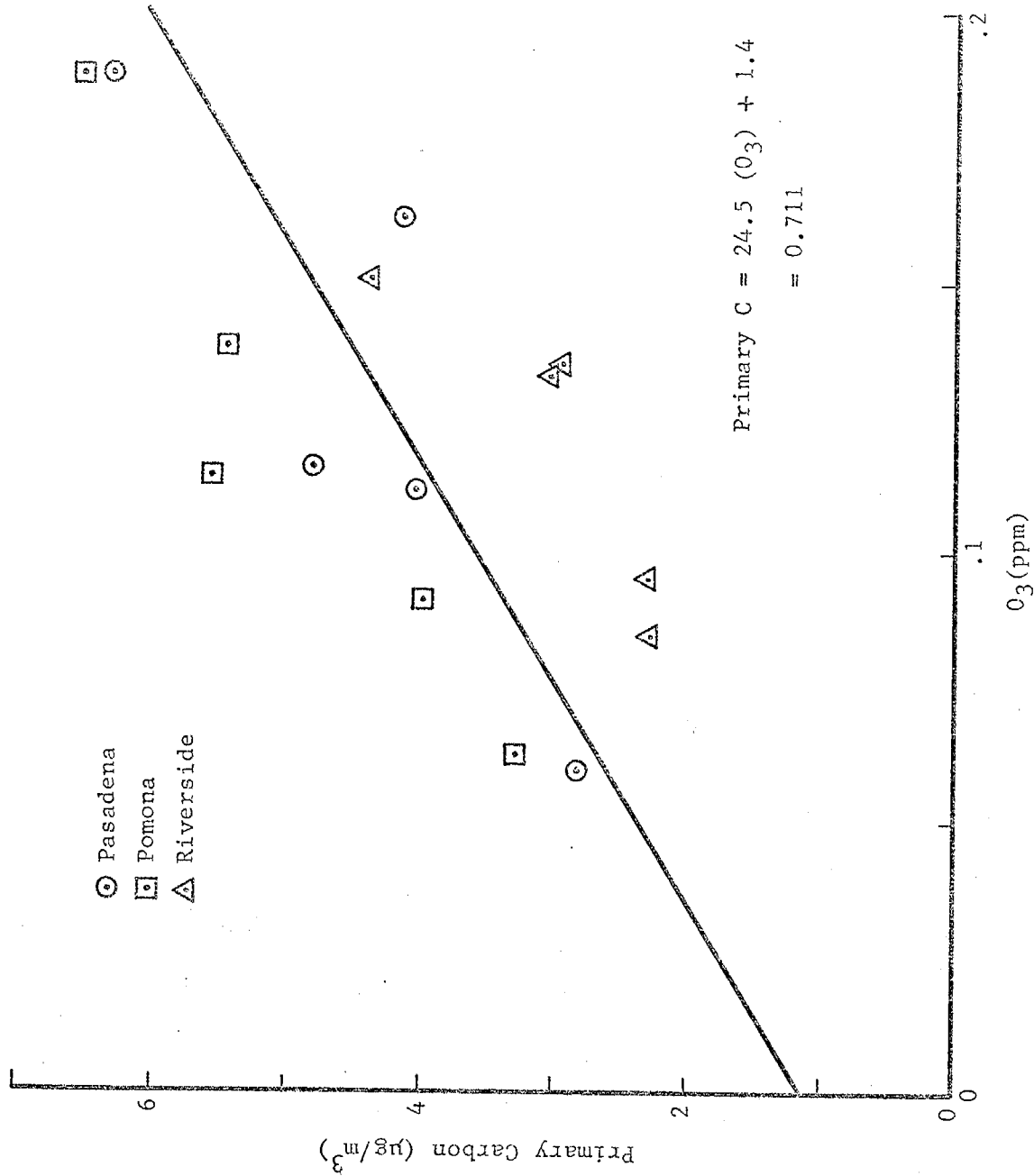
VIII. Correlations of Organic Aerosol Constituents with Ozone

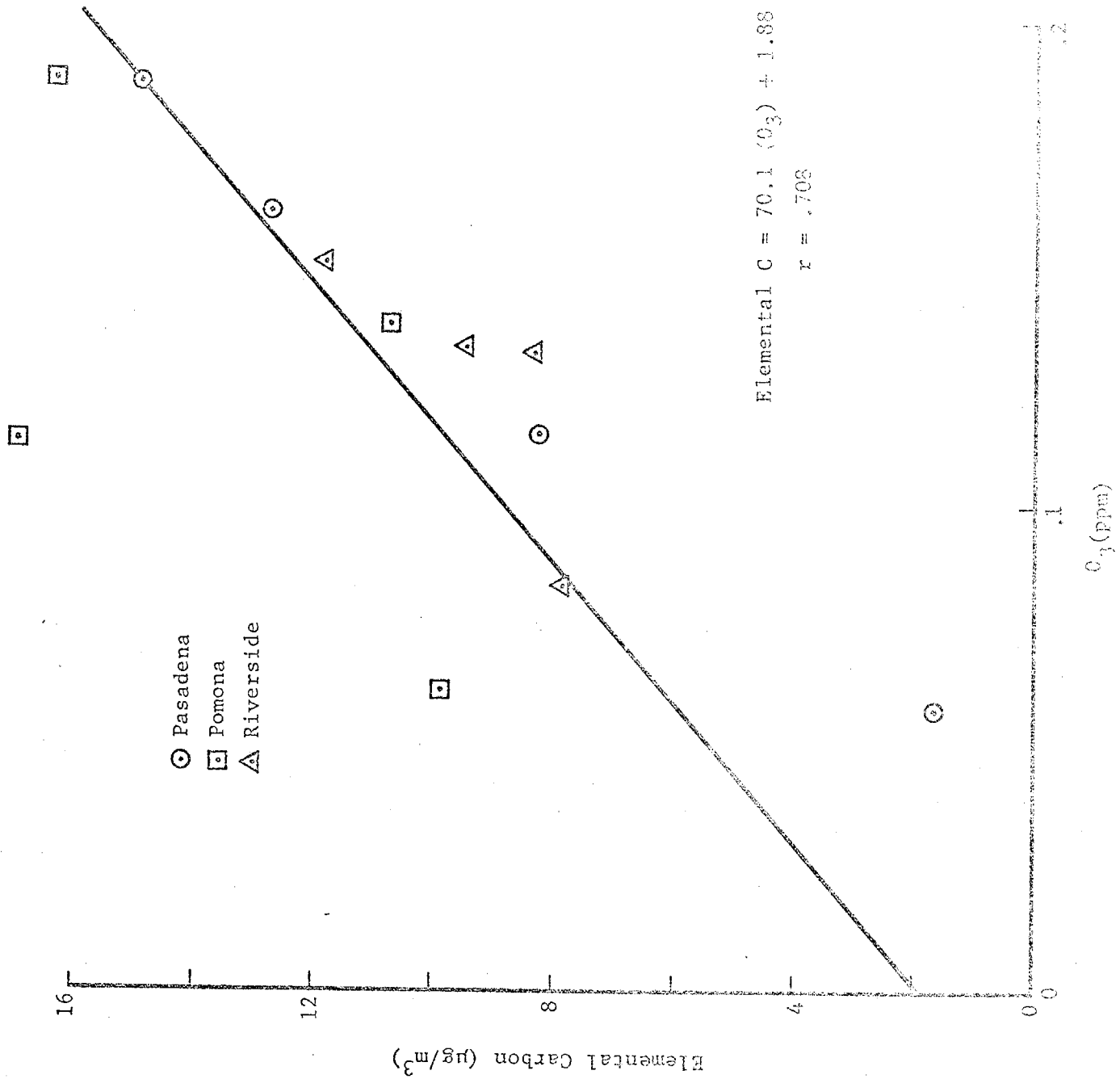
The preceding discussion of diurnal patterns suggest that correlations of both secondary and primary organic carbon with ozone should be expected. Correlations for carbonaceous fractions, with O_3 for the 14-hour samples are shown in Figures 25-27. All show correlation coefficients above 0.7. The best correlation is seen for secondary organic C ($r = 0.87$). The observed correlation between C_p and O_3 contrasts with ACHEX findings in which no correlation between these parameters was observed.



Secondary Carbon Against Mean Ozone Concentration For 14 Hour Samples

Figure 25





Elemental Carbon Against Mean Ozone Concentration For 14 Near Surface
Figure 21

Assuming that the observed correlation between O_3 and C_p is the result of meteorology (e.g., a reduced mixing volume increasing the concentration of all pollutants), then an approach to defining the C_s concentrations resulting from chemical conversions on the same day is to seek correlations between the C_s/C_p ratio and mean ozone. Such correlations are shown in Figure 28 separately by sampling site, again based on 14-hour sample results. The most notable observations are the small slopes observed (at Pomona the ratio actually decreases slightly with increasing O_3) and the generally higher ratio at Riverside compared to the other sites.

At least two factors probably contribute to these observations. First, it was noted that the cyclohexane extraction is not highly selective for primary organics. Thus, as the contribution of secondary organics increases, an increased amount of these materials are probably extracted into cyclohexane, thereby increasing the apparent C_p . Since C_s is large relative to C_p , a relatively small increase in C_s could substantially increase the observed C_p , thereby decreasing the C_s/C_p ratio. Secondly, the carry-over of aerosol from the preceding day could produce a fairly elevated C_s/C_p ratio in a sample collected on a day of relatively low ozone concentration.

It remains unclear why in the ACHEX studies with 24-hour samples, ozone correlated well with C_s and poorly with C_p in contrast to the current findings.

Correlations between O_3 , C_p and C_s were also evaluated using 2-hour samples. The results summarized in Table 18 show correlations of 0.6 - 0.9 at Pasadena for both C_p and C_s with ozone. At Pomona, excepting Episode D, the correlation coefficient for C_s with O_3 was 0.7 - 0.8 in contrast to -.2 to 0.4 for C_p . At Riverside the correlation is of doubtful significance for both C_p and C_s . In all cases, the slope is substantially greater for correlations with C_s .

IX. Sampling Errors in Filter Collection of Organic Particulate Matter

A. Background

Conceptually it is simple to define a particulate organic as a material existing in a condensed phase (liquid or solid) while suspended in the atmosphere. However, the sampling of such particles is difficult in practice. The vapor pressure of organic compounds in the atmosphere probably cover a range from > 1 atmosphere (i.e., completely gas phase at room temperature in the absence of absorbents) to essentially non-volatile. Both primary and secondary organics should exist in condensed as well as in gas phase, the proportions in each phase varying with the vapor pressure of the individual material, the quantity of the material in a given air mass and the degree to which it is adsorbed on materials of lower or negligible vapor pressure (e.g., soot).^{11, 23} If it is assumed that adsorption does, indeed, aid significantly in collection of otherwise volatile organics on filter samples, then the collection efficiency of filters for organics should increase as the filter becomes loaded.

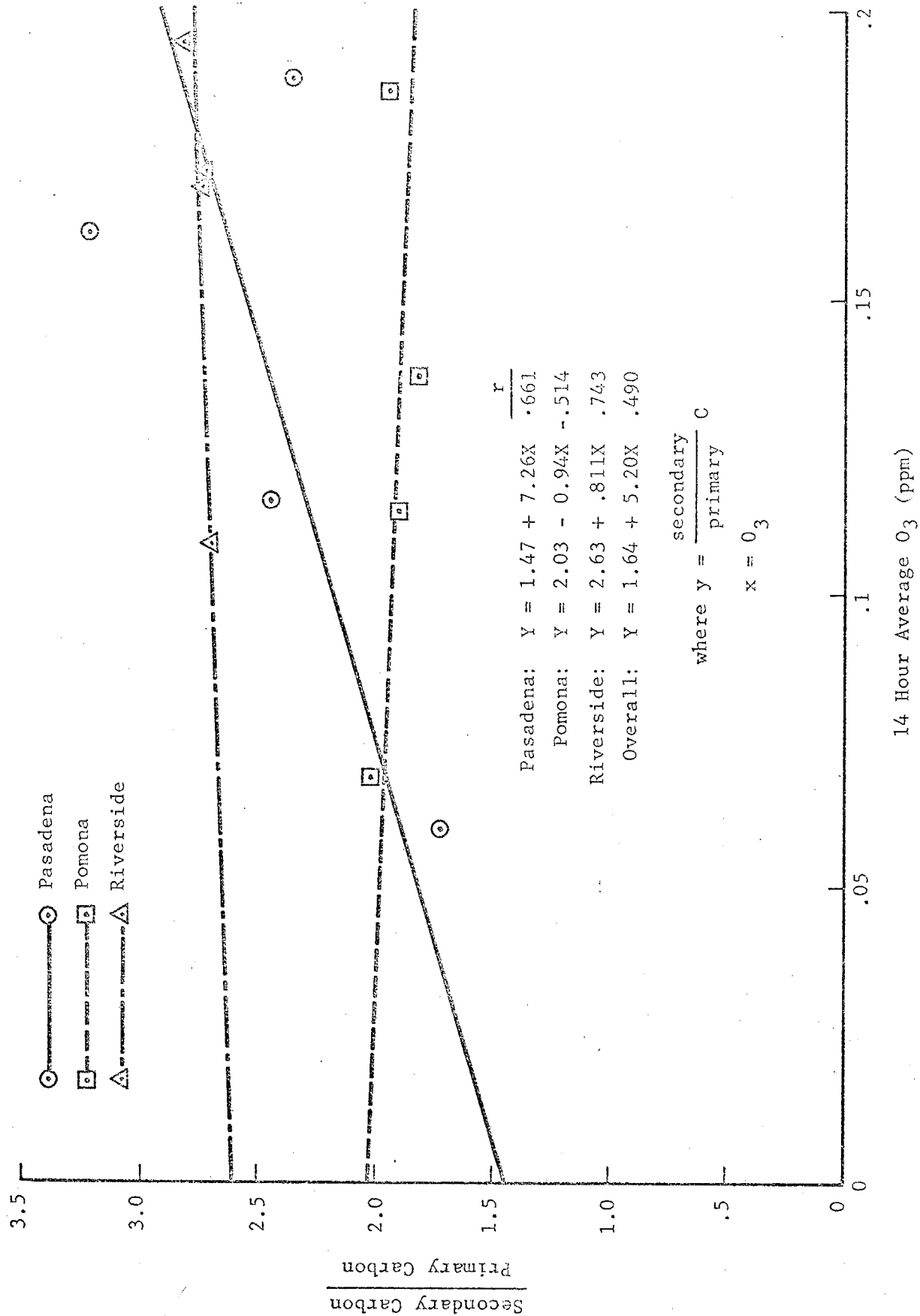


Figure 28 Ratio Secondary to Primary Carbon Against Mean Ozone For 14 Hour Samples.

Table 18

CORRELATION BETWEEN OZONE, PRIMARY AND SECONDARY ORGANIC
CARBON WITH TWO-HOUR SAMPLES

$$[y = a + b(O_3)]^a$$

Site	Episode	a		b		Correlation Coefficient, r	
		$\frac{C_p}{C_s}$	$\frac{C_s}{C_p}$	$\frac{C_p}{C_s}$	$\frac{C_s}{C_p}$	$\frac{C_p}{C_s}$	$\frac{C_s}{C_p}$
Pasadena	B	2.39	11.2	11.8	39.9	0.73	0.90
	C	1.91	9.91	14.3	36.9	0.77	0.63
	D	1.04	8.11	17.5	51.5	0.82	0.77
	E	1.06	5.17	7.79	46.7	0.89	0.84
Pomona	B	4.62	12.2	1.63	37.3	0.21	0.71
	C	3.75	7.24	5.74	79.5	0.18	0.73
	D	4.67	16.4	-3.13	3.72	-0.22	0.07
	E	1.76	4.66	6.36	82.7	0.44	0.81
Riverside	B	2.93	12.8	-7.39	15.7	-.09	0.47
	C	2.63	9.68	-3.89	16.2	-.23	0.24
	D	2.03	9.90	-1.07	10.5	-.23	0.49
	E	1.75	6.83	-1.14	26.6	-.09	0.49

a. Ozone concentration is in ppm and organic carbon, in $\mu\text{g}/\text{m}^3$.

Once collected on a filter, then both adsorbed and unadsorbed organics are subject to volatilization. Several studies support such losses. Della Fiorentina²⁴ concluded with respect to sampling organic aliphatic material on glass fiber filters that "at commonly used flow rates ... the composition of this material adsorbed on suspended material, varies greatly with the flow rate and duration of sampling: Most compounds with boiling temperatures lower than 300°C are progressively eliminated from the sample."

B. The Influence of Sampling Time in the Current Program

At each site, seven 2-hour hi-vol samples were collected side-by-side with a single 14-hour sample, permitting comparisons between samplers. Identical filter media were used in both samplers and flow rates were equivalent within 10%. Thus, any differences observed may be ascribed to the effects of sampling time. Table 10 compares the 14-hour samples to calculated 14-hour average results for TSP, total C, cyclohexane, benzene, and methanol-chloroform soluble C and elemental C.

Considering first TSP and total carbon (CEL), the calculated values consistently exceeds those observed at all sites. Of the carbonaceous fractions contributing to the total carbon, the methanol-chloroform soluble C (MCC), mean ratio 1.7, and elemental carbon, mean ratio 1.2, showed similar ratios. Since MCC and elemental carbon typically comprised 40-50% of the total carbon, their combined effect is sufficient to dominate over the opposite trends with CEC and BEC. Constituents other than carbonaceous materials apparently contribute to the high ratios for TSP since the total carbonaceous material (as carbon) was generally 20% or less of the TSP.* Artifact sulfate and nitrate may be contributors.

The obvious factor that can lead to ratios > 1.0 for carbonaceous materials is the loss of more volatile constituents not strongly adsorbed on other materials during the prolonged (14-hour) sampling consistent with Della Fiorentina's observations. This hypothesis can serve to rationalize the high ratios for MCC. However, if insoluble carbon provides a measure of elemental and polymeric carbon, then a ratio > 1.0 for elemental carbon cannot be explained by volatilization. Thus, only ratios > 1.2 (as observed for elemental carbon), for example, 1.7 for MCC, are here considered to be indicative of losses of organics due to volatilization. A more subtle potential source of ratios > 1.0 is loss of soluble organics from the 14-hour sample by precipitation from the extracting solvent.** However, such losses should generally increase

*If the carbonaceous material is assumed to be 50% carbon, then the carbonaceous material represents generally 40% or less of the TSP.

**It was noted in preliminary trials that if the 14-hour sample MCC extract was concentrated to < 10 ml, noticeable precipitation in the flask was observed. This was apparently due to residual benzene remaining from the previous extraction. Accordingly, the protocol was adjusted to keep greater volumes and the extracts from 14-hour samples were transferred to 25 ml rather than 10 ml volumetric flasks following Soxhlet extraction.

Table 19

COMPARISON OF OBSERVED AND CALCULATED^c 14-HOUR VALUES

Episode	Station	TSP	Calculated/Observed 14-Hour Analyses ^{a,b}				Elemental C
			CEL	CEC	BEC	MCC	
B	Pasadena	1.32	1.11 (.04)	.73 (.13)	.52 (.07)	1.60 (.18)	1.11 (.15)
B	Pomona	1.34	1.21 (.04)	.75 (.13)	.60 (.08)	1.98 (.22)	1.15 (.13)
B	Riverside	1.22	1.18 (.04)	.63 (.11)	.53 (.07)	1.52 (.17)	1.29 (.16)
C	Pasadena	1.41	1.12 (.04)	1.02 (.18)	.59 (.08)	1.59 (.18)	1.08 (.15)
C	Pomona	1.30	1.10 (.04)	.79 (.15)	.67 (.09)	1.85 (.21)	.92 (.11)
C	Riverside	1.39	1.26 (.05)	.66 (.13)	.68 (.09)	1.65 (.18)	1.21 (.15)
D	Pasadena	1.45	1.28 (.05)	.64 (.13)	.54 (.07)	1.45 (.16)	1.78 (.29)
D	Pomona	1.47	1.35 (.05)	.77 (.14)	.87 (.11)	1.72 (.19)	1.34 (.19)
D	Riverside	1.39	1.16 (.04)	.60 (.12)	.59 (.08)	1.58 (.18)	1.15 (.16)
E	Pasadena	1.41	1.34 (.06)	.54 (.12)	.65 (.09)	1.68 (.19)	1.46 (.19)
E	Pomona	1.14	1.09 (.04)	.67 (.13)	.59 (.08)	1.80 (.20)	.93 (.12)
E	Riverside	1.23	1.34 (.05)	1.12 (.15)	.58 (.08)	1.94 (.22)	1.36 (.15)
Mean Ratio		1.34	1.21	.74	.62	1.70	1.23

^aCEL = total carbon
 CEC = cyclohexane soluble C
 BEC = benzene soluble C
 MCC = methanol-chloroform soluble C
 Elemental C estimated by insoluble carbon, CEL-(BEC + MCC)

^bOne sigma value shown below each ratio.

^cCalculated from 7, 2-hour samples. - 70 -

with the amount of extracted organics in the sample. Since the amount of organics in the extract should increase with the atmospheric concentration of methanol-chloroform soluble organics, the absence of a correlation between MCC values (in $\mu\text{g}/\text{m}^3$) and ratios of calculated/observed 14-hour MCC suggests this is not the cause.

Ratios < 1.0 can also reflect both sampling and analytical errors. If initially collected carbonaceous material (e.g., soot or liquid phase organics) can function as absorbents for gas phase organics, such absorption should increase with loading, yielding elevated 14-hour values, hence, low ratios. The CEC and BEC are the fractions containing most of the hydrocarbons, materials which, in turn, have the highest vapor pressure for a given carbon number and, therefore, are likely to be the highest concentration gaseous organics.

Possible analytical errors in the solvent extraction-carbon analysis leading to ratios < 1.0 include:

1. Loss of particulate organics during Soxhlet extractions by volatilization at $60-80^\circ\text{C}$.
2. Loss of particulate organics during solvent evaporation at room temperature.
3. A negative and systematic error in carbon determination by combustion and gas chromatographic analysis.

Quality assurance studies described in Appendix D suggest that volatile losses during the vacuum treatment stage or organic solvent removal should be negligible. These QA studies also suggest errors in carbon determination are not the cause of the low ratios.

MSTA data can be used to evaluate losses of organics during extraction. Table 8 provided a comparison of the concentrations of selected species obtained by analysis of the original filter and of the total extractable levels by successive extractions with benzene and methanol-chloroform. The recovery of alkanes + alkenes by solvent extraction exceeded that by direct filter analysis. With alkylbenzenes, solvent extraction results, in two cases, are lower by ca. 25% but in one case they are higher by nearly a factor of two. We conclude that MSTA provides no clear indication of loss of organics by volatilization during extraction.

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